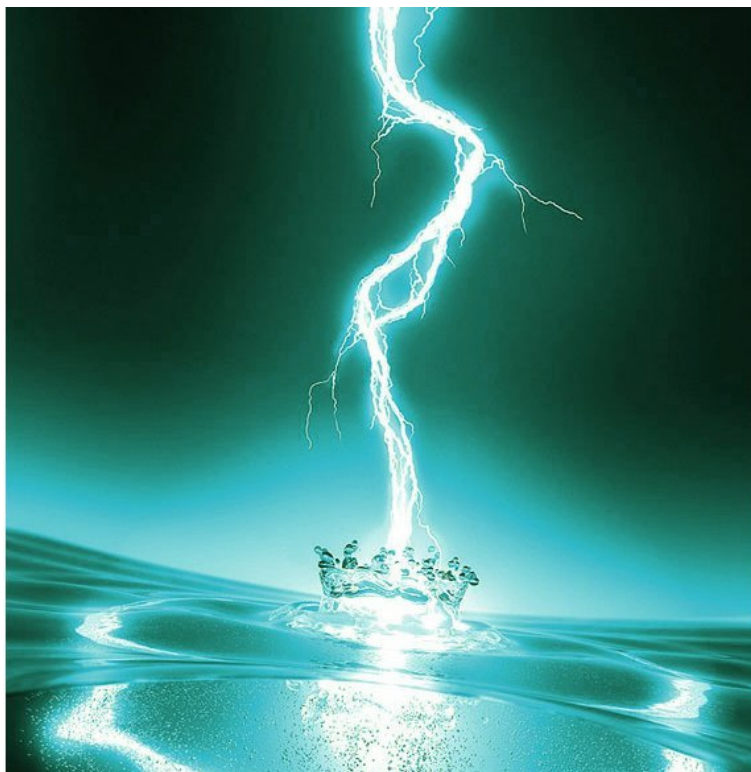


Technologies for Coal based Hydrogen and Electricity Co-production Power Plants with CO₂ Capture

C. García Cortés, E. Tzimas, S.D. Peteves



EUR 23661 EN - 2009

The Institute for Energy provides scientific and technical support for the conception, development, implementation and monitoring of community policies related to energy. Special emphasis is given to the security of energy supply and to sustainable and safe energy production.

European Commission
Joint Research Centre
Institute for Energy

Contact information

E-mail: carolina.garcia-cortes@jrc.nl

Tel.: +31 224 56 54 47

Fax: +31 224 56 56 23

<http://ie.jrc.ec.europa.eu/>

<http://www.jrc.ec.europa.eu/>

Legal Notice

Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use which might be made of this publication.

***Europe Direct is a service to help you find answers
to your questions about the European Union***

Freephone number (*):

00 800 6 7 8 9 10 11

(*) Certain mobile telephone operators do not allow access to 00 800 numbers or these calls may be billed.

A great deal of additional information on the European Union is available on the Internet. It can be accessed through the Europa server <http://europa.eu/>

JRC 49206

EUR 23661 EN
ISBN 978-92-79-11076-4
ISSN 1018-5593
DOI 10.2790/23969

Luxembourg: Office for Official Publications of the European Communities

© European Communities, 2009

Reproduction is authorised provided the source is acknowledged

Printed in Luxembourg

TABLE OF CONTENTS

LIST OF USED ABBREVIATIONS	7
LIST OF USED ABBREVIATIONS	7
1. ENERGY CONVERSION FACTORS	8
Energy	8
Power	8
2. ENERGY CONVERSION FACTORS FOR HYDROGEN	8
A. COAL	10
A.1. What is coal? Properties	10
A.2. Coal rank	12
A.3. Ash content	14
A.4. Coal in Europe: production and characteristics	16
B. COAL GASIFICATION	19
B.1. Introduction	19
B.2. Devolatilization mechanism and reactions	19
B.3. Coal pyrolysis gas	21
B.4. Gasification reactions	22
B.5. Gasification product gas	23
C. STATE OF THE ART OF THE TECHNOLOGY for HYDROGEN AND ELECTRICITY IGCC CO- PRODUCTION CYCLES	24
C.1. GASIFIERS	24
1.1.Types of gasifiers	24
1.2.Commercial technologies	30
1.3.Matching gasifiers to coals	35
C.2. WATER GAS SHIFT REACTION (WGS)	37
2.1.Clean Gas Shift	37
2.2.Raw Gas Shift	37
C.3. Cold/Warm gas cleanup	38
3.1.Particulate removal	38
3.2.Acid Gas Removal	41
C.4. HOT GAS CLEANUP	51
4.1.Particulate removal	51
4.2.Chlorine compounds removal	52
4.3.Hot Gas Desulphurization (HGD)	53
C.4. CO ₂ CAPTURE	55
C.5. OXYGEN SEPARATION TECHNOLOGIES	63
C.6. HYDROGEN SEPARATION TECHNOLOGIES	65
C.7. GAS TURBINES (GT)	66
REFERENCES	69

LIST OF FIGURES

Figure 1 Coal composition basis [1]	11
Figure 2 Coal rank [6]	12
Figure 3 Anthracite structure [7]	13
Figure 4 Bituminous coal structure [7]	13
Figure 5 Coal clasification by ash content	15
Figure 6 Primary energy consumption of fossil fuels 2003-2030 [16]	16
Figure 7 Lignite and hard coal production in Europe [17]	16
Figure 8 Energy power production in EU [17]	17
Figure 9 Gasification mechanism	19
Figure 10 Coal devolatilization [18]	20
Figure 11 Pyrolysis mechanism (adapted from [19])	20
Figure 12 Depolymerization reactions [21]	20
Figure 13 Coal pyrolysis gas composition [25]	21
Figure 14 Exemple of gasification phase diagram coal Illinois #6 dry feed. [29]	23
Figure 15 Membrane wall [31]	24
Figure 16 Fixed bed gasifier [35]	25
Figure 17 Updraft gasifier [36]	25
Figure 18 Downdraft gasifier [36]	26
Figure 19 Crossdraft gasifier [36]	26
Figure 20 Fluidized bed gasifier [35]	26
Figure 21 Bubbling bed gasifier [36]	27
Figure 22 Circulating bed gasifier [36]	27
Figure 23 Transport reactor [37]	27
Figure 24 Entrained flow gasifier [35]	28
Figure 25 Down and up flow gasifiers	28
Figure 26 Texaco radiant cooler [40]	32
Figure 27 Texaco water quench [40]	30
Figure 28 Shell Gasifier [40]	30
Figure 29 Conoco-Phillips gasifier [42]	31
Figure 30 Siemens gasifier	31
Figure 31 HTW Gasifier [40]	32
Figure 32 KRW gasifier [40]	32
Figure 33 IDGCC gasifier [46]	33
Figure 34 Lurgi CFB gasifier [47]	33
Figure 35 KBR gasifier [28]	33
Figure 36 U-gas Gasifier [28]	33
Figure 37 BGL gasifier [49]	34
Figure 38 Lurgi gasifier Source: Sasol	34
Figure 39 Fabric filter [55]	38
Figure 40 Packed bed, fluidised bed and Venturi scrubbers [57]	39
Figure 41 Gravity Settler [54]	40
Figure 42 Cyclone [54]	40
Figure 43 Electrostatic Precipitator [54]	40
Figure 44 Gas sweetening with amines Source: Lurgi	45
Figure 45 Selexol process Source: UOP LLC	49
Figure 46 Catalyst for SCR at different temperatures [78]	57
Figure 47 PSA Operation [87]	59
Figure 48 Chemical looping combustion	63
Figure 49 Oxygen separation capacity [108]	63
Figure 50 ASU [109]	64
Figure 51 Membrane configuration [108]	64
Figure 52 Ion transport membranes configuration [108]	65
Figure 53 Flame temperature of Hydrogen	67

LIST OF TABLES

Table 1 Coal calorific value [9]	13
Table 2 Typical coal composition by rank [9].....	14
Table 3 Main mineral compounds in coal ash [10]	14
Table 4 Ash content by rank.....	14
Table 5 Variations in coal ash composition [13]	14
Table 6 Sapropelic coal composition [15].....	15
Table 7 Coal production in Europe [16]	16
Table 8 German coal properties [16].....	17
Table 9 Polish coal properties [16].....	17
Table 10 Czech coal properties [16].....	17
Table 11 Coal proved reserves at end 2007[17]	18
Table 12 Coal production in EU [17]	18
Table 13:Pyrolysis products	21
Table 14 Syngas composition for different dry feed gasification processes. Coal (Illinois#6) . Oxidant: Oxygen. [28]	23
Table 15 Fixed bed gasifiers by syngas movement	25
Table 16 Moving bed gasifiers by bed movement.....	27
Table 17 Entrained flow gasifiers by syngas movement	28
Table 18 Gasifiers Main characteristics and operating conditions[38][39]	29
Table 19 Commercial entrained flow gasifiers.....	31
Table 20 Commercial entrained flow gasifiers	32
Table 21 Commercial entrained flow gasifiers for a coal Illinois #6.....	32
Table 22 Fluidized bed gasifiers.....	34
Table 23 Fluidized bed gasifiers.....	34
Table 24 Fix bed gasifiers	34
Table 25 Matching coals to gasifiers [52]	36
Table 26 Performance of commercial WGS [53]	37
Table 27 Particulate removal from cold gas [54]	38
Table 28 Fabric filter materials [54].....	39
Table 29 Gas desulphurization methods.....	41
Table 30 Desulphurization/decarbonization processes (S: Selective NS: Non-selective)	44
Table 31 High temperature fabric filters [70].....	51
Table 32 Decarbonization processes	56
Table 33 Relative Strength of Adsorption of Typical Impurities [58].....	59
Table 34 Relative membrane permeabilities [91].....	60
Table 35 Inorganic membranes	61
Table 36 Hydrogen selective membranes. Adapted from [96]	62
Table 37 Hydrogen separation methods . Adapted from [110].....	65
Table 38 Hydrogen vs Methane properties [112]	66

LIST OF USED ABBREVIATIONS

AB: absorption
AD: adsorption
AF: ash free
AFT: ash fusion temperature
ASU: air separation unit
BFBG: bubbling fluidized bed gasifier
CGE: cold gas efficiency
CFBG: circulating fluidized bed gasifier
CV: calorific value
D: dry
EFG: entrained flow gasifier
FT: Fluid Temperature
GT: Gas turbine
HGI: Hardgrove Grindability Index
HRSG: heat recovery steam generator
HT: Hemispherical temperature
IDT: initial deformation temperature
IGCC: integrated gasification combined cycle
LOX: liquid oxygen
MFV: minimum fluidizing velocity
MMF: mineral matter free
NG: natural gas
NS: non selective
PAH: polycyclic aromatic hydrocarbon
PSA: pressure swing adsorption
REF: reference
S: selective
ST: Steam turbine
T: temperature
TCV: temperature of critical viscosity
TIT: Turbine Inlet Temperature
TOT: Turbine outlet temperature
VIGV: variable guide inlet vanes
VM: volatile matter
VOL: volume

1. ENERGY CONVERSION FACTORS

Volume

1 Nm³ = 35.315 cubic ft (scf)

Pressure

1 Mpa = 145 psi = 9.9 atm

1 atm = 14.696 psi = 1.01325 bar

1000 psi = 68.9 bar = 68.05 atm

Energy

1 kWh = 3.6 MJ

1 BTU = 1.05506 kJ

1 Therm = 105.506 MJ

1 cal = 4.187 J

1 kcal = 4.185 kJ

Power

1 horsepower = 0.7457 kW

1 boiler hp = 9.803 kW

1 BTU/hr = 0.293071 W

1 kcal/hr = 1.163 W

2. ENERGY CONVERSION FACTORS FOR HYDROGEN

Power

1 kW = 10.5 scf per hr

1 MW = 10,500 scf per hr = 297.5 Nm³ per hr = 3.6 GJ per hr

1 GW = 10.5 Mscf per hr = 297,500 Nm³ per hr = 3,600 GJ per hr

1 TW = 10.5 Bscf per hr = 297.5 MNm³ per hr =

1 Mscf per hr = 327 mmBtu per hr

Energy

1 GJ = 277.8 kWh = 2,915 scf = 75.36 Nm³ = 10⁹ J

1 kWh = 10.5 scf = 0.298 Nm³ = 0.95 mmBtu

1 MWh = 10,500 scf = 297.5 Nm³ = 3.6 GJ

1 GWh = 10.5 Mscf = 297,500 Nm³ = 3,600 GJ = 3,430 mmBtu

1 TWh = 10.5 Bscf = 297.5 MNm³ = 3.6 PJ

1 kg H₂ = 11.08 NM³ = 128.8 MJ (HHV) = 135,100 Btu = 375.6 scf

10⁶ scf = 343 GJ = 26,850 Nm³

1 lb H₂ = 5.04 Nm³ = 0.0585 GJ (HHV) = 16.26 kWh = 187.8 scf

1 Nm³ H₂ = 0.09 kg = 3.361 kWh

1 scf H₂ = 343 kJ = 325 Btu (HHV)

1 kWh = 3,410 Btu

1 scf natural gas = 1,010 Btu

Kilo = 10³, Mega = 10⁶, Giga = 10⁹, Tera = 10¹², Peta = 10¹⁵, Quad = 10¹⁵, Exa = 10¹⁸

EXECUTIVE SUMMARY

The reliable and secure operation of the power systems requires the continuous balancing of the production and consumption resources connected to the electricity network. The temporal and geographical variability of demand and supply, to a certain extent amplified by the increasing penetration of renewable intermittent resources (mainly wind) and by the development of electricity market, calls for fast-reacting and flexible energy generating units - possibly flanked by a further deployment of energy storage technologies and demand management techniques - capable to compensate for power unbalances and able to quickly react to changing market strategies.

The combination of two products for different markets allows tailored electricity production by switching from one product to the other. Besides, it lets the units that are common to both processes to operate at full load. Continuous operating conditions favour the investment amortization and protect the main machines from thermal load oscillations.

Integrated Gasification Combined Cycle (IGCC) plants allow the combination of the production of hydrogen and electricity because coal gasification process produces a syngas that can be used for the production of both commodities. This combination can be done mainly thanks to the shift reaction that converts the carbon monoxide contained in the syngas into hydrogen and carbon dioxide. A hydrogen and electricity power plant has been denominated as HYPOGEN. Therefore, the IGCC plant, relying upon a coal gasification process that allows the co-production of electricity and hydrogen, can provide combined quotas of these two energy carriers in a wide range of power outputs. Hence, it is able to operate in a flexible mode. "Flexible operation" refers to the capacity of a plant to operate under certain previously selected conditions

Hydrogen and electricity are expected to play an increasingly important role as interchangeable energy carriers in a future sustainable energy economy. Both wells can be co-produced from different fuels as coal or natural gas. This study is based on coal transformation because it is abundant, it has a wide geographical distribution, and its price is relatively stable. Besides, the Green Paper 2006 of the European Commission alerts over the dependence risk in case of a natural gas based electricity generation in Europe. However, in the context of climate change the Green Paper 2006 states that the use of coal for electricity production is only sustainable if accompanied by commercialised carbon sequestration and clean coal technologies on an EU level.

The first question that has to be answered in order to develop a HYPOGEN plant is that of the technology available that would be suitable for such a concept. This report starts by reviewing the basics of the coal gasification process and continues by trying to map all the technological options currently available in the market as well as possible future trends. Besides, it offers an overview of the operating conditions and outputs of each process in order to provide the modeller with a useful information tool enabling an easier analysis of compatibilities and implementation of the model.

A. COAL

A.1. What is coal? Properties

Coal is a complex sedimentary rock derived from plant remains. It is the result of the organic material accumulation and its physic and chemical transformation via the great pressures and temperatures uphold in the beds.

It is an extremely complex and heterogeneous material consisting of a composite of:

- Hydrocarbons (referred to as volatiles)
- Non-volatile combustible material (referred to as char; this is mostly carbon in solid form)
- Ash
- Water

The most important properties for coals evaluations are:

1. *Calorific value*: It's the amount of chemical energy stored in a coal that is released as thermal energy upon combustion. It is directly related to rank.
The relationships between calorific value dry basis(CV(D), kJ/kg) and ash (dry basis, percent), and calorific value moist mineral matter free(CV(MMMF), kJ/kg) and equilibrium moisture (MEQ) percent were determined to be:

$$\begin{aligned}CV(D) &= 29262 - 286(\text{Ash}[D]) \\ CV(MMMF) &= 31816 - 442(\text{MEQ}).\end{aligned}$$

2. *Moisture*: The moisture content of the bulk as sampled is referred to as *total moisture*. Moisture held within the coal itself after air-drying (in equilibrium with environmental moisture) is known as *inherent moisture* or *bed moisture* and varies systematically with change in rank. The moisture lost via air-drying is the *Surface moisture* .

In general we can distinguish the following moisture types:

Surface moisture: water held on the surface of coal particles.

Inherent moisture

Hygroscopic moisture: water held by capillary action within the microfractures of the coal
Decomposition moisture: water held within the coal's decomposed organic compounds
Mineral moisture: water which comprises part of the crystal structure of hydrous silicates such as clays

Moisture reduces the coal heat of combustion [1]

3. *Ash content*: Ash content of coal are the impurities consisting of hydrated aluminium silicates, iron pyrites, calcium and magnesium carbonates, alkali chlorides, and other incombustible residue left after coal is burnt. It represents the bulk mineral matter after carbon, oxygen, sulphur and water (including from clays) has been driven off during combustion. Ash increases the weight of coal and can affect the burning characteristics. Ash content is measured as a percent by weight of coal on an "as received" or a "dry" (moisture-free) basis.
4. *Volatile matter*: It is a mixture of vapours and gases released during the pyrolysis of coal (mainly CO, CO₂, H₂O and hydrocarbons including tars involved during the decomposition of the coal structure). In general, volatile matter decreases when increases the coal rank.
5. *Fixed carbon*: Fixed carbon is the part of the total carbon that remains when coal is heated in a closed vessel until all volatile matter is driven off. [2]
It is calculated as: $100 - (\% \text{moisture} + \% \text{volatile matter} + \% \text{ash})$
The volatile matter value decreases with increasing rank of coal.

The composition of the coals can be given in different basies (as received, air dried, as free..) depending on the consideration of moisture and/or ash and/or mineral matter contained in the fuel

A general view of the different basis to express the coal composition can be found in the figure below:

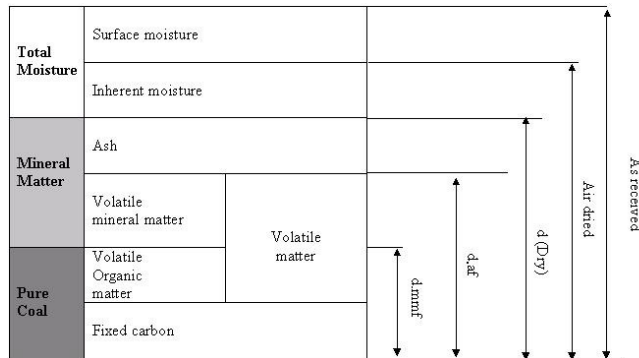


Figure 1 Coal composition basis [1]

d,af: dry, ash free
d, mmf: dry, mineral mater free

6. *Agglomerating character*: Agglomeration describes the caking properties of coal. Agglomerating character is determined by examination and testing of the residue when a small powdered sample is heated to 950 degrees centigrade under specified conditions. If the sample is "agglomerating," the residue will be coherent, show swelling or cell structure, and be capable of supporting a 500-gram weight without pulverizing[2]. Bituminous coals are commonly agglomerating while anthracite, lignite and subbituminous coals are non-agglomerating.
7. *Sulphur content*: One of the elements present in varying quantities in coal that contributes to environmental degradation when coal is burned, because of the formation of corrosive acids during the combustion. Sulphur may occur in three possible forms:

Organic sulphur: Chemically combined with the carbon of the pure coal.
Pyritic sulphur: Combined with iron as iron pyrites.
Sufate sulphur: Combined as a sulphate.

Low sulphur content varies from 0.1 to 1.0 % wt, medium content values are between 1% and 3% and over 3% of sulphur , coals are considered to have a high content.

8. *Ash fusion temperature*: Ash fusion temperatures give an indication of the softening and melting behaviour of fuel ash. The behaviour of a coal's ash residue at high temperature is a critical factor in selecting coals for steam power generation. The ash fusion temperature depends on the composition of the ash and in general is increased by the presence of certain elements as SiO_2 and/or Al_2O_3 .

It can be defined as well as the temperatures where triangular pyramids (Cones) prepared from coal ash attain and pass through certain defined stages of fusing and flow when heated at a specified rate in controlled, idly reducing and oxidizing atmospheres. Each one of these stages has a proper reference temperature:

Initial Deformation Temperature of Ash : (IDT) : Where the first rounding of the cone occurred.

Softening Temperature (ST) is the temperature where cone is fused down to a spherical lump. Is when agglomeration starts

Hemispherical Temperature (HT) is when the cone has fused down to a hemisphere.,

Fluid temperature (FT) is where the fused mass has spread out nearly flat layer.[3]

9. *Porosity*: The pores give coal a high surface area and appreciable volume of pore space, allowing access to a significant fraction of organic material [4]
10. *Reactivity*: A measure of the rate at which residual char from a given coal will react with CO₂ under arbitrary and fixed conditions of temperature and gas composition. The term is expressed as a weight loss per unit time or time to achieve a fixed weight loss. It affects the combustion efficiency, the ability of fuels to create NOx, the temperature distribution in the furnace etc...

Reactivity decreases with the rank and increases with the oxygen functional groups content of the fuel [5].

11. *Hardness*: ability to resist penetration, indentation, or scratching
12. *Density*: mass contained within a unit volume under specified conditions.
13. *Grindability*: The grindability of a coal is a measure of its resistance to crushing. Indicates the ease of pulverizing a coal in comparison to a reference coal. This index is helpful in estimating mill capacity. Two factors affecting grindability are the moisture and ash contents of a coal. The two most common methods for determining this index are the Hardgrove Grindability Method and Ball Mill Grindability Method.

The Hardgrove Grindability index is a measurement of the relative ease of pulverizing a coal in comparison with a standard coal chosen as 100 grindability. The higher the grindability index, the easier the coal is to grind. In general, coals with a low index (lignites and anthracites) are more resistant to grinding than are bituminous. Thus, Hardgrove grindability index is rank dependent and increases as does rank, although anthracites have low Hardgrove grindability indices[2]

A.2. Coal rank

Coals are classified considering the degree of metamorphism. Many chemical and physical properties change during this progression.

The *rank* refers to the degree of carbonisation undergone by the organic matter. It is determined by evaluation of the *rank parameters*: moisture content, specific energy, reflectance of vitrinite or volatile matter content.

Figure 2 Coal rank [6]

Coal Types and Peat			Total Water Content (%)	Energy Content af* (kJ/kg)	Volatiles maf** (%)	Vitrinite Reflection in oil (%)
UN-ECE	USA (ASTM)	Germany (DIN)				
Peat	Peat	Torf				
Ortho-Lignite	Lignite	WEICHBRAUNKOHL	75	6,700		
Meta-Lignite		Mattbraunkohle	35	16,500		0.3
Subbituminous Coal	Sub-bituminous Coal	Glanzbraunkohle	25	19,000		0.45
Bituminous Coal	High Volatile Bituminous Coal	Flammkohle	10	25,000	45	0.65
	Medium Vol. Bitumin. Coal	Gasflammkohle			40	0.75
	Low Vol. Bitumin. Coal	Gaskohle			35	1.0
	Semi-Anthracite	Fettkohle		36,000	28	1.2
	Anthracite	Eßkohle			19	1.6
		Magerkohle			14	1.9
		Anthrazit	3	36,000	10	2.2

af* = ash-free maf** = moisture ash-free

UN-ECE: Ortho-Lignite up to 10,000 kJ/kg, Meta-Lignite up to 16,000 kJ/kg, Subbituminous Coal up to 19,000 kJ/kg, Bituminous Coal up to 25,000 kJ/kg, Anthracite up to 36,000 kJ/kg

Source: FGT

Low rank

Medium rank

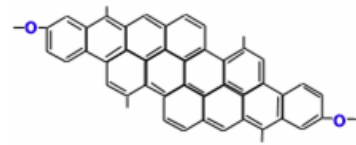
High rank coals

Anthracite, Sub-bituminous coals and lignite have a non-agglomerating character

Anthracite: Very hard and dense coal with high Hydrogen content (between 92% and 98%) and contains the fewest impurities of all coals. Anthracite difficultly ignites and it does it with an extremely hot, blue flame and very little smoke. Anthracite coal has a very low level of volatile components and a high percentage of fixed carbon. It does not form coke when heated.

Anthracite structure is characterized by high density of aromatics rings. It has a low content of functional groups. Links are mostly aromatic-aromatic.

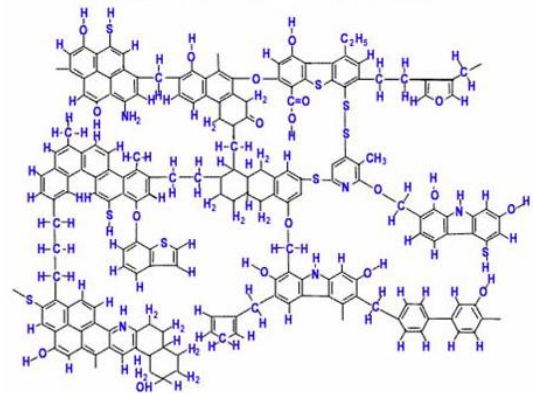
Figure 3 Anthracite structure [7]



Bituminous coal: dense, banded dull and glossy black coal with relatively hardness contains bitumen (tar-like substance). It contains a high percentage of volatile matter and it ignites easily with a smoky long yellow flame. It exhibit agglomerating and caking behaviour, making this coal useful for making coke.

Bituminous coal structure is characterized by the aliphatic, ether and sissile biphenyl cross links and for the hydroxyl functional groups. Aromatic carbons are incorporated in rings ranging from two to four condensed rings [8]

Figure 4 Bituminous coal structure [7]



Sub-bituminous coal: dull, dark brown to black coal. It is soft and crumbly. It has relatively low density and high water content. It is susceptible to spontaneous combustion.

Its structure is similar to the bituminous coal but with larger rings containing more oxygen based functional groups (carboxyl, hydroxyl...). The cross links are mainly hydrogen and ether bonds.

Aromatics carbon are incorporated in one to three condensed rings.

Lignite: Is the lowest rank coal. It is soft, brownish-black coal and it easily burns with a long and smoky flame. It contains a high moisture and volatile matter. It is generally referred to as brown coal.

Lignite has many oxygen containing functional groups. It contains many hydrogen bonds and some salty bonds.

Physical properties change with rank but there is no single property that changes uniformly over the complete range. Furthermore, a coal's type and grade influence many of the measured rank parameters.

The calorific value of the coal increases with an increase in rank to a maximum in the sub-bituminous range and then tends to decline slightly in the anthracites.

	CV MJ/Kg (daf)
Lignite	<30
Sub-Bituminous	30-31
Bituminous	32-37
Anthracite	<34.5

Table 1 Coal calorific value [9]

	VM % (daf)	C % (daf)	H% (daf)	O% (daf)	Moisture%	Ash (%)
Lignite	>46.7	<73	4,5	>21	>25%	30-50%
Sub-Bituminous	25-50	73-78	6	16-19.2%	14-25%	20-30%
Bituminous	14-50	77-91	5,3	2.5-13.5	5-14%	10-20%
Anthracite	<14	>91	2,5	<2.8	1-5%	<10%

Table 2 Typical coal composition by rank [9]

VM: Volatile mater

A.3. Ash content

The ash is the inert material of the coal derived from the mineral matter in it. It reduces the heat value of the coal.

Main mineral compounds in coal are:

Mineral Name	Major Oxide Components
Quartz	SiO ₂
Kaolinite	SiO ₂ , Al ₂ O ₃
Illite	SiO ₂ , Al ₂ O ₃ , K ₂ O
Montmorillonite	SiO ₂ , Al ₂ O ₃ , CaO, Na ₂ O
Pyrite	Fe ₂ O ₃ , SO ₃
Calcite	CaO
Dolomite	CaO, MgO
Sodium Carboxylate *	Na ₂ O
Calcium Carboxylate *	CaO

Table 3 Main mineral compounds in coal ash [10]

* - represents organically bound elements

Low-rank coals contain large amounts of Na, Mg, Ca, K and Sr as salts of organic acid group, chelates or as mineral grains [11]. Carboxyl and associated oxygen groups decreases with the rank. Higher-rank coals contains mainly mineral grains of kaolinite, quartz, illite, calcite and pyrite. However, considering the major mineral in the ash is enough to describe sufficiently the coal ash chemistry [4].

Ash analysis is important in order to dispose fly ashes clean facilities and predict slagging and corrosion behaviour. Ash melting point will help to determine operational conditions in combustion and gasification processes. However, "ash melting point" refers to the temperature when viscosity decreases. Under the melting point, minority minerals have already melted. As the temperature increases, minerals with higher melting temperature melt and ash becomes less viscous. Melted compounds react and act as molten glass and dissolve the non-molten materials like quartz and other minerals.

Clay minerals that contain significant amounts of iron, calcium sodium or potassium cause low melting temperatures (1000-1200°C), favouring slagging, which is also intensified by the pyrite, clays (silicium and aluminium oxides) and alkalis (CaO, MgO) interaction with aluminosilicates to form low viscosity ways [12]

Ash content and composition varies with the rank of the coal

Table 4 Ash content by rank

	Ash (%)
Lignite	30-50%
Sub-Bituminous	20-30%
Bituminous	10-20%
Anthracite	<10%

Rank	Composition, %									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Ash
<i>Crandall (1972)</i>										
Anthracite	48-68	25-44	2-10	1.0-2	0.2-4	0.2-1	—	—	0.1-1	4-19
Bituminous	7-68	4-39	2-44	0.5-4	1.0-36	0.1-4	0.2-3	0.2-4	0.1-323	32
Subbituminous	17-58	4-35	3-19	0.6-2	2.0-52	0.5-8	—	—	3.0-163	16
Lignite	6-40	4-26	1-34	0.0-0.8	12.0-52	2.8-140	28	0.1-1.38	3-324	19
<i>Meikle (1975)</i>										
Bituminous	30-55	10-35	10-40	1.0-3	0.0-15	0.0-5	1.0-5	0.0-3	—	—
Lignite	20-41	10-18	7-16	1.0-3	20.0-40	2.0-11	0.5-0	0.5-0	—	—
<i>Endell (1958)</i>										
Lignite (Fortuna)	4-40	2-4	14-16	—	49.0-55	9.0-15	—	—	8.0-12	—

Table 5 Variations in coal ash composition [13]

Attending to the ash content, coals can be classified in different grades. Grade refers to the mineral proportion, being 50% the ash limit for coals, 80% the limit for middlings and 100% for shales.

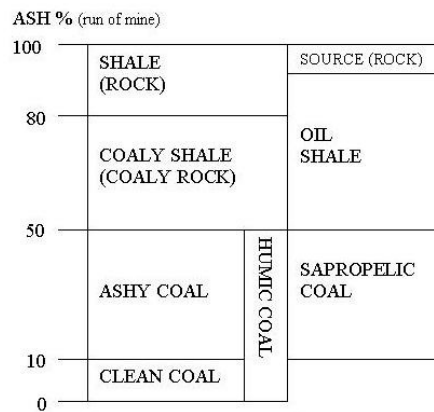


Figure 5 Coal clasification by ash content

Therefore, the grades of the properly called "coals" (<50%ash) are:

Sapropelic coal: Non-banded coals that have their origin in lakes. They are formed by the degradation of standard coal-peat swamp materials and the addition of other remains, such as algae and wind- or water-borne spores. Sapropelic coals are thin and lenticular and they often occur at the bases and tops of seams [14]

Sapropelic coals can be classified by rank:

- *Sapropel*: Unlithified dark, pulpy, fine organic mud containing identifiable concentrations of algae and microspores.
- *Coorongite*: Rubber-like, highly resilient structureless algal deposit.
- *Sapropelic lignite*: macroscopically similar to humic lignite.
- *Sapropelic coal*: fine grained, dark coloured.

Carbon content % dry ash free	Volatile content %	Rank stages of sapropelic coal series
<60	>63	Sapropel coorongite
60-70	52-63	Sapropelic lignite
>70	<52	Sapropelic coal

Table 6 Sapropelic coal composition [15]

Humic coal: the organic material passed through peat stage. It has low hydrogen content and it has its origin in:

- Organic debris accumulates in stagnant, swamps (do not want oxidation and decomposition)
- Cyclic sedimentation,
- The precursor is peat.
- Processes in peat bogs: Accumulation; Compaction; Bacterial and fungal "attack"; Coalification

A.4. Coal in Europe: production and characteristics

The increasing demand of energy and the limited fuel resources are exposing the EU to a complicate future energy scenario in which the energy supply hang on the fuel importations. In the next 20 or 30 years imports could cover up to a 70% of the energetic consumption, and, in the case of Natural Gas, this proportion is increased up to 85%. The Green paper 2006 of the European Commission alerts over the dependence risk in case of a Natural Gas based electricity generation in Europe.

On the other hand, instability of petrol prices boosts electricity prices making more complicate the situation of the consumers in Europe.

Coal supply is especially secure because coal is mined in many countries throughout the world and trade operates in accordance with free market principles, what ensure more stable prices. Abundant and distributed coal reserves warrant the European energy supply.

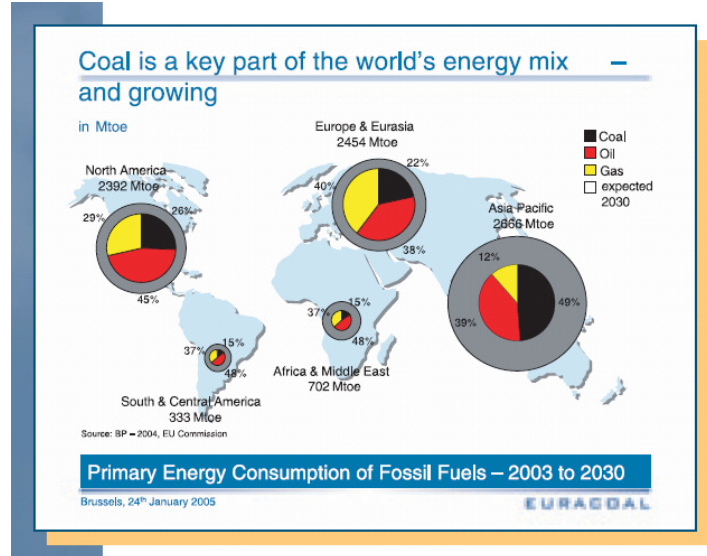


Figure 6 Primary energy consumption of fossil fuels 2003-2030 [16]

However an important improvement of efficiencies, clean coal technologies and CO₂ capture has to be done in order to allow the coal to be an environmental friendly energetic option.

The three main requirements that coal has to fulfil to be a sustainable energy source are:

1. Security of supply
2. Competitiveness
3. Environmental compatibility

European and world production levels guarantee the security of supply and price predictability.

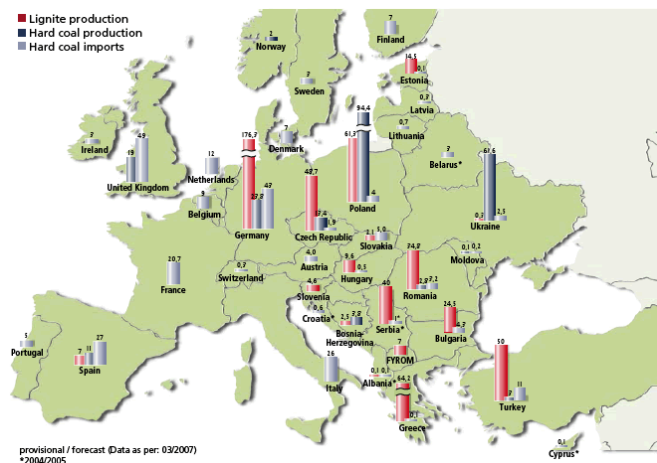


Figure 7 Lignite and hard coal production in Europe [17]

In the EU-25 there are installed 3005TWh, where 664.5 TWh are produced from Hard Coal and 265.5TWh from lignite.

The net power imports are 1.5TWh.
(2004 data)

Coal production in selected countries 2004			
	Hard Coal	Lignite and Brown Coal	Total
Austria	–	0.2	0.2
Bosnia	–	8.7	8.7
Bulgaria	3.2	23.7	26.9
Czech Republic	13.3	48.8	62.1
France	0.2	–	0.2
Germany	29.2	181.9	211.1
Greece	–	71.9	71.9
Hungary	0.3	11.8	12.1
Poland	99.2	61.1	160.3
Romania	3.7	31.6	35.3
Serbia	–	33.9	33.9
Slovak Republic	–	3.0	3.0
Slovenia	–	4.8	4.8
Spain	12.3	8.2	20.5
Turkey	2.9	67	69.9
UK	25.1	–	25.1

Table 1: Coal production in selected countries 2004 (Mt)
Source: EURACOAL

Table 7 Coal production in Europe [16]

The main coal producers in Europe are

- **Germany**

Table 8 German coal properties [16]

Selected Coal Quality Data		
<i>Calorific Value</i> Hard Coal	kJ/kg	27,400 – 33,000
<i>Calorific Value</i> Lignite	kJ/kg	7,800 – 11,300
<i>Ash content</i> Hard Coal	%	6 – 7
<i>Ash content</i> Lignite	%	1.5 – 22.0
<i>Water content</i> Hard Coal	%	8 – 9
<i>Water content</i> Lignite	%	40 – 60
<i>Sulphur content</i> Hard Coal	%	0.8 – 1.0
<i>Sulphur content</i> Lignite	%	0.15 – 2.8

- **Poland**

Table 9 Polish coal properties [16]

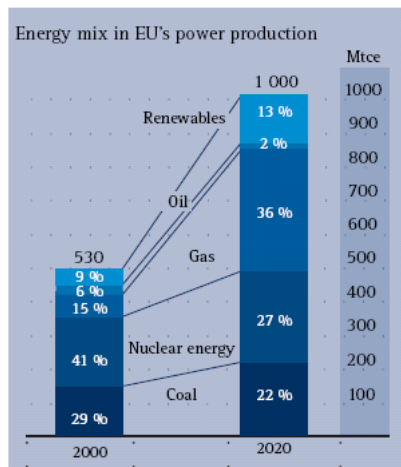
Selected Coal Quality Data		
<i>Calorific Value</i> Hard Coal	kJ/kg	18,000 – 30,000
<i>Calorific Value</i> Lignite		7,400 – 10,300
<i>Ash content</i> Hard Coal	%	7.0 – 30.0
<i>Ash content</i> Lignite	%	7.2 – 16.0
<i>Water content</i> Hard Coal	%	7.0 – 11.0
<i>Water content</i> Lignite	%	50.0 – 52.0
<i>Sulphur content</i> Hard Coal	%	0.6 – 1.2
<i>Sulphur content</i> Lignite	%	0.2 – 1.4

- **Czech Republic**

Table 10 Czech coal properties [16]

Selected Coal Quality Data		
<i>Calorific Value</i> Hard Coal	kJ/kg	21,520 – 29,000
<i>Calorific Value</i> Lignite	kJ/kg	11,200 – 19,900
<i>Ash content</i> Hard Coal	%	6.9 – 29.6
<i>Ash content</i> Lignite	%	19.5 – 12.0
<i>Water content</i> Hard Coal	%	7.9 – 10.2
<i>Water content</i> Lignite	%	26.8 – 39.5
<i>Sulphur content</i> Hard Coal	%	0.4 – 0.6
<i>Sulphur content</i> Lignite	%	0.6 – 1.8

The competitiveness will be ensured for a cost-efficient energy supply at favourable prices on a permanent basis.



Important investments have to be done in order to achieve further advances in coal based power generation technologies. Higher efficiencies will rise the power production while coal consumption and, therefore, CO₂ emissions, decreases. Since RWE, power generation efficiencies should improve from a 4% (for hard coal based technologies) to 8% (for lignite based technologies) in the next 15 years

Figure 8 Energy power production in EU [17]

Coal: Proved reserves at end 2007					
Million tonnes	Anthracite and bituminous	Sub-bituminous and Lignite	Total	Share of total (world basis)	R/P ratio
Bulgaria	5	1991	1996	0.2%	66
Czech Republic	1373	2828	4501	0.5%	72
Germany	152	6556	6708	0.8%	33
Greece	-	3900	3900	0.5%	62
Hungary	199	3103	3302	0.4%	336
Poland	6012	1490	7502	0.9%	51
Romania	12	410	422	<0.05%	12
Spain	200	330	530	0.1%	29
United Kingdom	155	-	155	<0.05%	9

Table 11 Coal proved reserves at end 2007[17]

Coal: Production *	2007	Change 2007 over 2006	2007 Share of total
Bulgaria	5.1	10%	0.2%
Czech Republic	23.6	-0.5%	0.8%
France	0.1	-40%	<0.05%
Germany	51.5	2.5%	1.6%
Greece	8.2	-3.6%	0.3%
Hungary	2.0	-1.4%	0.1%
Poland	62.3	-7%	2%
Romania	7.4	1.3%	0.2%
Spain	6.0	-4.0%	0.2%
United Kingdom	10.4	-8.1%	0.3%

Table 12 Coal production in EU [17]

B. COAL GASIFICATION

B.1. Introduction

Gasification is a process in which the thermal decomposition occurs in oxidant atmosphere (air or pure oxygen) with a controlled C/O ratio in order to keep the reduction conditions of the global process. Oxidation exothermic reactions afford the necessary heat for the endothermic reactions and higher temperatures than in the pyrolysis process are reached in the reactor.

Coal first pyrolyzes with the heat, and light volatile hydrocarbons, tars and phenols are released. Pyrolysis char reacts with gaseous reactants to release gases, tar vapours and a solid residue made up by char and ash. The main product of the gasification is a gas consisting of CO, H₂, and some CH₄ and CO₂. Steam or water (coal-water slurry feeding) can be added in order to increase the amount of Hydrogen produced in the gas.

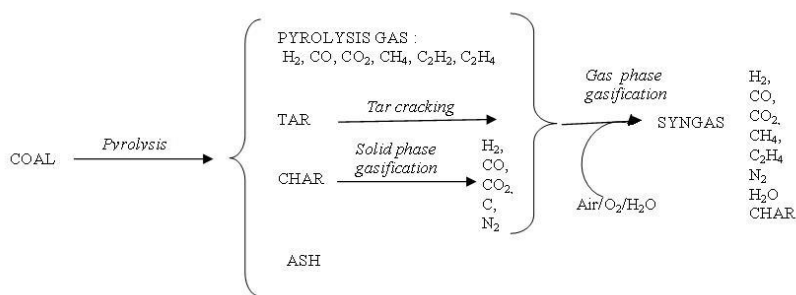


Figure 9 Gasification mechanism

If air is used as oxidant atmosphere the product has a lower calorific value than if pure oxygen is used because the nitrogen in the air dilutes the product gas. On the other hand, the use of pure oxygen means the needing of an Air Separation Unit, which increases the cost of the installation and implies a consumption of energy thus, the decrease the global energy efficiency.

B.2. Devolatilization mechanism and reactions

Pyrolysis is an endothermic thermal decomposition process in an inert atmosphere that results in variable amounts of syngas, liquids (tars and oils) and a solid carbonaceous residue referred to as char. The quantity of each product generated depends on the pyrolysis conditions being the more influential variables the temperature, the heating rate, the particle size, the pressure, the residence time and of course, the fuel type.

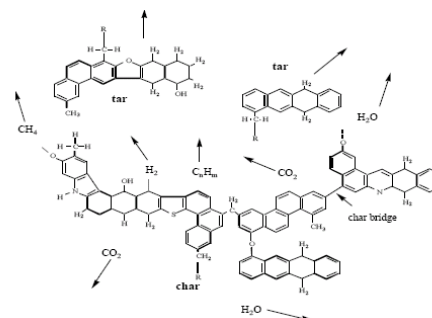
Coal is a large polymeric matrix mostly made up by polynuclear aromatic ring systems linked one to the other by aliphatic or ether bridges or by bi-aryl links. Bridges containing oxygen are weak while single bonds between aromatic clusters (or char links) are relatively stable.

As the temperature of the raw coal increases, weak bonds break liberating some light gases and decomposing the macromolecular structure which forms liquid components referred to as metaplast. Parallel to coal structure disintegration, char bonds stabilize during this stage. The further transformations undergone by the metaplast with a progressive heating are conditioned by operating conditions as well as by coal rank.

In the pyrolysis mechanism we can distinguish in two steps: a primary and a secondary pyrolysis.

During the *primary pyrolysis* depolymerization and cross-linking reactions occur. During the temperature rising (up to 740°C) bonds linking aromatic clusters break creating large fragments detached from the macromolecule (*metaplast*). Lower molecular weight fragments vaporize (tar) and the rest is cross-linked again to the coal structure. Tars are defined as volatiles which condense at room temperature.

Figure 10 Coal devolatilization [18]

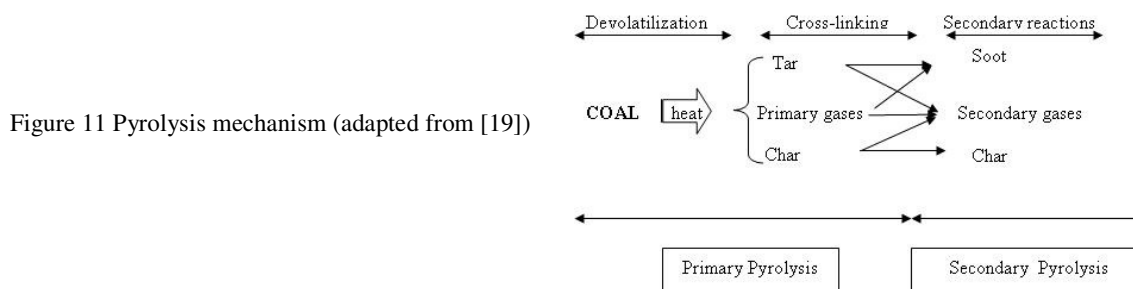


Some CO, CO₂, H₂O and light hydrocarbons appear as a result of the detachment of some functional groups linked to the aromatic clusters.

During the *secondary pyrolysis*, some reactions occur in the gas phase being the tar the main reactant at this stage. The temperature rises over 927 °C and side chains attached to the aromatic clusters in the tar are released as light gases (CO, CO₂, H₂O and light hydrocarbons) and HCN NH₃ SO₂ COS...[19]

The temperature in which the chemical reactions occur varies significantly with the heating rate and the coal type .

Devolatilization chemistry is highly complex because of the parallel cleavage and cross-linking reactions occurring in the reactor. Besides, the kinetics of the reactions depends not only on the coal composition but on the operating temperature, pressure, heating rate, particle size...

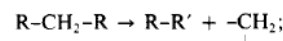


Depolymerization reactions: H.Jüntgen [20] studied the kinetics of the pyrolysis in order to establish the relation between the depolymerisation reaction kinetics and the chemical composition of the coal. He concluded that the C-C bonds at the bridges linking aromatic clusters were weaker than those of the aromatic rings. Therefore, the cleavage of these bonds happens at moderate temperature. During the cracking of the bridges, radicals liberated (mainly -CH₂ and -O-) recombine to form aliphatic gas molecules as CH₄ and H₂O (saturation reaction) which diffuse out of the coal particle. Larger ring fragments hydrogenate to medium molecular weight tars while high molecular weight aromatic clusters condense to coke by liberating gaseous hydrogen. The hydroaromatic hydrogen is consumed in the saturation reactions to produce CH₄ or H₂O and in the tar production

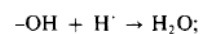
Figure 12 Depolymerization reactions [21]

At higher temperatures heterocyclic oxygen groups crack producing CO and H₂O.

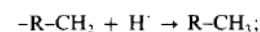
Cracking:



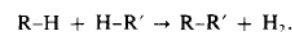
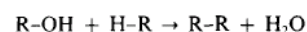
Saturation:



Tar production:



Condensation reaction:



The cleavage of methyls groups split off from aromatic rings and cleavage of biaryl ethers results in methane and carbon monoxide formation. [22]

Cross-linking reactions: The metaplast is repolymerized via the cross-linking reactions to form char. These reactions avoid the further evolution of tars whose yield stops at a given high temperature.

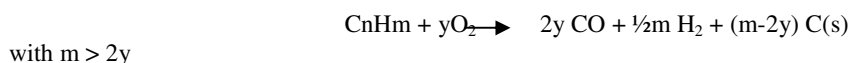
Cross-linking reactions control the tar yield and molecular weight distribution, fluidity, and char surface area and reactivity.

Cross-linking reactions are rank-dependent, occurring in lignite at lower temperatures than in bituminous coal. At the cross-linking reaction temperature, tars in lignite have not started to evolve while those in bituminous coal have already reach its maximum evolution [23].

In low rank coals, cross-linking reactions occurs at the same time that the evolution of CO₂ while for high rank coals they are concurrent with CH₄ evolution [24]

Secondary reactions: Tar is the main reactant of this period because its high reactivity (instability) and its high concentration in the gas phase.

Tars aromatic hydrocarbons (PAH and phenols) mainly polymerize to coke (soot) with the evolution of hydrogen or crack to lower molecular weigh hydrocarbons and hydrogen



B.3. Coal pyrolysis gas

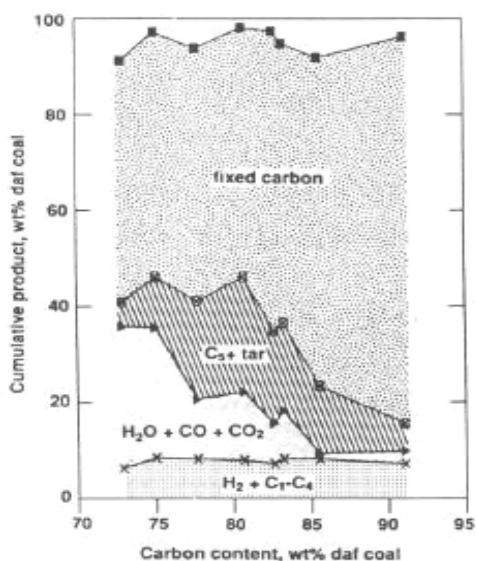
Main product or pyrolysis is a volatile fraction composed by gases and tars and a solid residue referred as coke or char depending on the plasticity of the coal , which consists in a slurry of ashes and non-reacted carbon.

The volatile component of coal released during volatilization conditions can account for as much as 50% of the heating value of the coal and for up to 70% of the total coal weight loss. We can distinguish two types of volatiles:

1. Light gases
2. Tars

The percentage of each type contained in the volatile yield, varies with the rank.

Much of the high volatile matter of low rank coals comes from thermal cracking of C-O- C ether bridges and carboxylic acids (-COOH) and esters, releasing products. In higher rank coals, such ether linkages become less important (because oxygen levels are lower) and fewer volatile products are generated as the coal is heated [25]



	Gas yield	Tar yield
Low rank coals	HIGH	LOW
High volatile bituminous	MODERATE	HIGH
High rank coals	LOW	MODERATE OR LOW

Table 13:Pyrolysis products

Figure 13 Coal pyrolysis gas composition [25]

1. Light gases: H_2O , CH_4 , CO_2 , CO , H_2 , C_2H_6 , C_3H_8 , C_4H_{10} , N_2
 2. Tars: tar comprises all organic components having a molecular in the range 200-2000 existing as a liquid at room temperature. Benzene is not considered to be a tar. The composition of the tars varies with the coal and volatilization conditions and they can be classified by the degree of evolution which depends on the temperature:

- a. **Low temperature tars**: Thin oily layer with low specific gravity due to their low aromatic compounds density. The main characteristic is that they are produced under 550°C and does not contain any naphthalene. Naphthalene is only formed at temperatures upwards of 750°C . The typical constituents of primary tar are paraffins, olefins, naphtenes and phenols [26].
- b. **High temperature tars**: High temperature tars are mainly integrated by olefins, paraffin hydrocarbons and cyclic hydro-aromatic structures High temperature allows the evolution of tars to more aromatic compounds as PAH

B.4. Gasification reactions

- **Reactions in the solid phase:**

- Partial oxidation
$$\text{C} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO} \quad \Delta h^\circ_{298} = -123 \text{ kJ/mol}$$
- Combustion
$$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2 \quad \Delta h^\circ_{298} = -406 \text{ kJ/mol}$$
- Gasification with steam
$$\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2 \quad \Delta h^\circ_{298} = +118.9 \text{ kJ/mol}$$
$$\text{C} + 2 \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 2\text{H}_2 \quad \Delta h^\circ_{298} = +78 \text{ kJ/mol}$$
- Boudouard
$$\text{C} + \text{CO}_2 \longrightarrow 2\text{CO} \quad \Delta h^\circ_{298} = +159.7 \text{ kJ/mol}$$
- Hydrogenation
$$\text{C} + 2 \text{H}_2 \longrightarrow \text{CH}_4 \quad \Delta h^\circ_{298} = -88.4 \text{ kJ/mol}$$

- **Reactions in the gas phase:**

- Partial oxidation
$$\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2 \quad \Delta h^\circ_{298} = -283 \text{ kJ/mol}$$
- Water shift
$$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta h^\circ_{298} = -40.9 \text{ kJ/mol}$$
- Methanation
$$\text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta h^\circ_{298} = -206.3 \text{ kJ/mol}$$
- Hydrogen oxydation
$$\frac{1}{2} \text{O}_2 + \text{H}_2 \longrightarrow \text{H}_2\text{O} \quad \Delta h^\circ_{298} = -285,8 \text{ kJ/mol}$$
$$\text{CO} + 2\text{H}_2 \longrightarrow \text{CH}_4 + \text{CO}_2 \quad \Delta h^\circ_{298} = -247 \text{ kJ/mol}$$

These reactions are controlled by the O/C ratio into the gasifier, by the maximum temperature and pressure and by the heating ratio.

Most of the oxygen consumed in the hydrogen and carbon combustion and in the carbon partial oxidation. These reactions are highly exothermic and provide the heat necessary for the gasification reactions.

Main gasification reactions are the gasification reactions in the solid phase where the reaction of carbon with steam at temperatures and low pressures results in hydrogen and carbon dioxide. These reactions are highly endothermic and have high activation energy and the rate is proportional to the steam partial pressure [4] .

The Boudouard reaction is endothermic and, in absence of catalyst, occurs very slowly at temperatures under 1000°K . The reaction is inhibited by the CO produced in the partial oxidation and carbon gasification with steam (*Le Chatelier* principle)

CO water shift reaction and gasification with steam in the solid phase are the sole reactions providing hydrogen. Hydrogen is consumed at the hydrogenation reaction but it occurs very slowly except under high pressure.

Water shift reaction is important for hydrogen production. This reaction is used to adjust the H_2/CO ratio in the gas. As it is an exothermic reaction it occurs at low temperatures in presence of a catalyst and pressure has not effect on increasing hydrogen yield. [27]

The methanation reaction proceeds very slowly and at low temperatures except if the pressure is high enough or a specific catalyst is used.

B.5. Gasification product gas

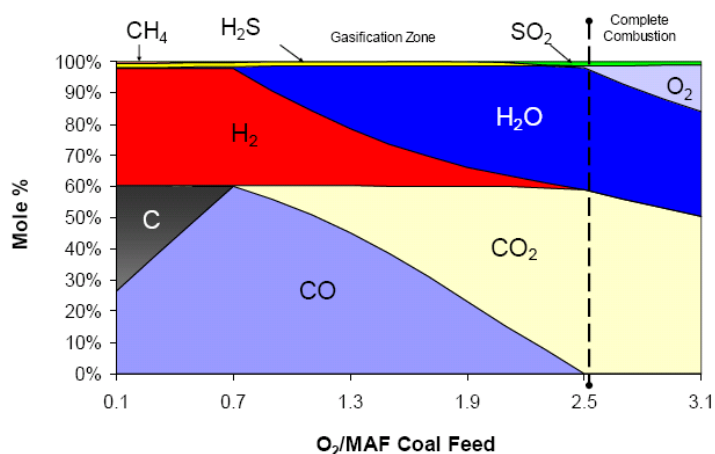
The heating value of the produced gas depends mainly on the oxidant agent used in the gasification. The use of pure oxygen produces a medium-rich gas that can be used for power generation in integrated gasification combined cycle power plants (IGCC) or in fuel cells or for chemical synthesis of NH_3 , Methanol, substitutive natural gas (SNG), alcohols or liquid fuels. However, the use of air results in a lower calorific power gas that can be used for power generation in IGCC power plants, in a boiler for steam production and as a fuel for smelting and iron or reduction applications [27].

But the chemical composition of the gas depends on many other factors as coal rank, coal preparation and particle size, heating rate, coal and gas residence time, coal feeding system (dry or slurry), coal-reactant flow geometry , mineral removal system (dry ash or slag), heat generation (direct or indirect gasification), operating temperature and pressure and gasifier type.

Raw gas comp	H ₂ O	H ₂	CO	CO ₂	CH ₄	COS	H ₂ S	NH ₃ +HCN	N ₂ +Ar
Technology	%vol	%vol	%vol	%vol	%vol	%vol	%vol	%vol	%vol
Entrained flow	2	26.7	63.1	1.5	0.03	0.1	1.3	0.02	5.2
Moving bed	5.1	52.2	29.5	5.6	4.4	0.04	0.9	0.5	1.5
Fluidized bed	4.4	27.7	54.6	4.7	5.8	0.1	1.3	0.08	1.7

Table 14 Syngas composition for different dry feed gasification processes. Coal (Illinois#6) . Oxidant: Oxygen. [28]

Figure 14 Exemple of gasification phase diagram coal Illinois #6 dry feed. [29]



C. STATE OF THE ART OF THE TECHNOLOGY for HYDROGEN AND ELECTRICITY IGCC CO-PRODUCTION CYCLES

C.1. GASIFIERS

1.1. Types of gasifiers

Gasifiers are usually classified by the flow regime inside the reactor. There are three main categories:

1. Fixed or Moving bed gasifiers
2. Fluidized bed gasifiers
3. Entrained flow gasifiers

Each type of gasifier depending on the operation characteristics can be classified in:

- Pressurized and non-pressurized
- Autothermal or allothermal

Autothermal gasification: The heat required for gasification reactions is supplied by partial oxidation of the syngas. Air or a steam/oxygen mixture are used as oxidant agents.

Allothermal gasification: The heat required for gasification reactions is afforded by an external source. Steam is used as the gasification agent.

- Using air or oxygen as gasificant agent
- Slagging, dry ash or agglomerate.

Gasification slag is vitrified ash containing some unconverted carbon

Agglomerate: If operating temperature is over the Initial Deformation Temperature of Ash (IDT), it starts to melt and get sticky creating agglomerates.

Dry ash: The ash has not melt because the operating temperature of the gasifier is under the IDT.

- Refractory lined or membrane walled:

Refractory lining: It isolates the reactor and helps to keep the temperature. It can work under high temperatures up to 1600°C. Main failure problems are due to chemical corrosion caused by the silica compounds contained in coal ashes. Besides, sodium compounds and other alkali matter diffuse into the refractory lining. In addition to the chemical attack, physical erosion can be caused by the molten slag flowing down the wall [30]

Membrane wall: It consists of high-pressure tubes in which steam is generated. A portion of the molten slag forms a layer coating the inner surface of the gasifier. Therefore, the liquid slag does not come in contact with the wall avoiding corrosion and erosion problems. [30]

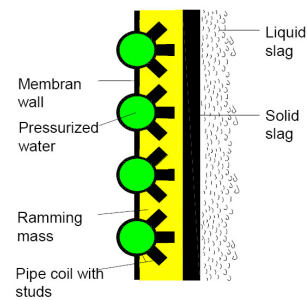


Figure 15 Membrane wall [31]

FIXED OR MOVING BED GASIFIERS

Most of these gasifiers are used with oxygen and steam which are injected into the bottom of the reactor while the fuel is fed at the top, producing a counter-current flow. The raw fuel gas flows relatively slowly upward through the bed of coal feed and cools by drying the coal. This process allows a lower syngas temperature at the output (400 °C -500 °C), avoiding the needing of an expensive cooling system.

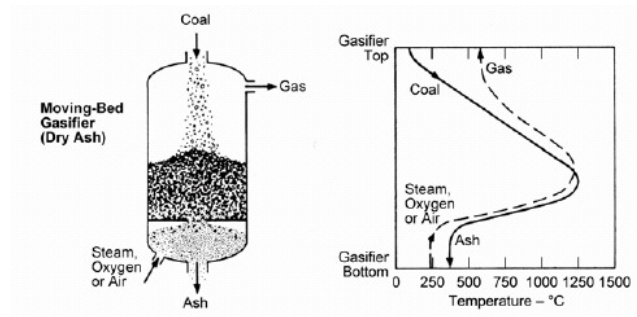
Ash may be either dry or slag depending on the steam/oxygen ratio and the melting characteristics of the mineral matter. Slagging ash gasifiers use a higher ratio; therefore the temperature at the combustion zone is much lower. This is the reason why reactive carbons as lignite are more suitable for dry ash gasifiers

Temperature varies from 400°C at the top to 800 °C - 1400 °C at the bottom for slagging gasifiers and 1000 °C for dry ash gasifiers.

This type of gasifier accepts only solid fuels with a size from 5 to 80 mm. Minor fragments have to be briquetted before entering into the gasifier. The requirement of a sized coal is one of the main disadvantages of this technology.

The residence time is long (15 to 60 min) for high pressure steam/oxygen gasifiers and several hours for atmospheric pressure steam/air gasifiers [32]

Figure 16 Fixed bed gasifier [35]



The syngas outlet temperature is low (400°C to 600°C) depending on the coal moisture content.

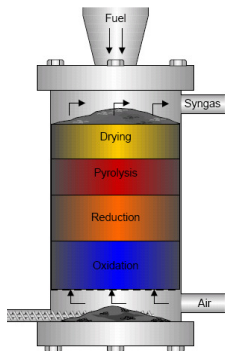
The produced syngas has a high heating value due to the high methane content and the consumption of oxygen in the reactor is very low. As a result, the thermal efficiency of the process is very high. The main disadvantage of this technology is that the size is limited because it is difficult to reach a large fuel bed with uniform temperature distribution [36]

Attending to the relative movement of the syngas flow respect to the fuel flow, fixed bed gasifiers can be classified in Updraft, Downdraft or Crossdraft

	UPDRAFT	DOWNDRAFT	CROSSDRAFT
Gasification agent	Air (Oxygen or steam mixtures can be used)	Air (Steam can be used)	Air
Operating temperatures(°C)	300-1000	500-1000	300-1000

Table 15 Fixed bed gasifiers by syngas movement

UPDRAFT GASIFIERS: It is a vertical reactor where the oxidant gas enters at the bottom while the fuel is fed at the top. The syngas leaves at the top. As fuel flow and gas flow movement is opposed, this type of gasifiers is usually called "counter-current" gasifiers. Moving beds gasifiers are always counter-current.



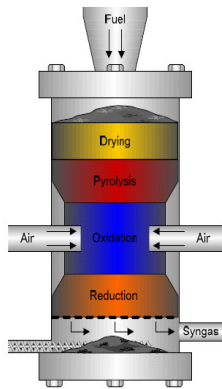
Fuel bed lies on a grate at the lowest part. The ash is deposited at the bottom.

The main disadvantage of this technology is that as the raw gas traverse through the devolatilization and drying zone, it contains a significant amount of tars, phenols, oils and low boiling point hydrocarbons that have been trapped upwards by the gas before traversing the gasification zone. Thus, they have not reached the necessary temperature for cracking. These tars are separated by washing the gas and recycled to the gasifier.

Other inconvenience is that the high temperatures reached near the ash deposit can cause its fusion. The main advantage is its simplicity and the low temperature of the outgoing gas (which means high efficiency of the equipment). [36]

Figure 17 Updraft gasifier [36]

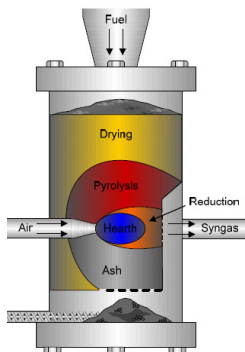
DOWNDRAFT GASIFIERS: In this reactor, the fuel is fed at the top and the oxidant agent enters in the oxidation zone, but the raw gas leaves the gasifier at the bottom. Thus, fuel and gas flows have parallel movement. This is why this type of gasifier is called "co-current".



The high tar compounds formed at the pyrolysis stage, reach the very hot oxidation region, where they are broken down into low tars producing, at the reduction zone, additional gases. The main disadvantage of this technology is the low heating value of the gas because of the high level of oxidation. This results in a high amount of CO₂ contained in the gas. Other negative factor is the high temperature of the exit gas, which reduces the efficiency. Slagging problems can appear because of the high temperatures in the reactor. Its advantages are low level of tars in the gas and the low-cost of the technology [36]

Figure 18 Downdraft gasifier [36]

CROSSDRAFT GASIFIER: Syngas is leaving the reactor at the medium from the opposite side of the air input. Fuel is fed by the top.



The ash bin, fire and reduction zone are separated. This characteristic limits the type of fuel for operation to low ash fuels such as wood, charcoal, and coke

The low syngas quality, high tar content, low CO₂ reduction are the main disadvantages of this technology, besides the high temperature of the gas [36]. However its design is simple

Figure 19 Crossdraft gasifier [36]

FLUIDIZED BED GASIFIERS

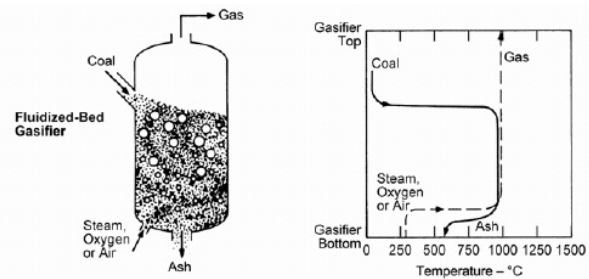
This type of gasifier has great fuel and load flexibility and can only operate with solid crushed fuels (0.5-5mm). The residence time is about 5-100s but it can be longer. Quartz or dolomite sand bed are usually used to increase the heat exchange between the fuel particles and the kinetics and mixture. [36]

Oxygen and steam consumption is low and operating temperatures are constant (900°-1100°C) and below ash melting temperatures. As a consequence, incomplete carbon conversion leads to lower cold gas efficiency. In hybrid systems, coal is first gasified in a fluidised bed and char is combusted in a fluidized bed combustor. This increases the carbon conversion.

Gasifying agent is usually air. It has to be fed with a minimum fluidizing velocity (MFV) to ensure the bubbling of the bed. For velocity values higher than the MFV the particles of the bed will flow up causing a circulating bed.

The low temperatures avoid thermal stress in the reactor. Ash can be dry or agglomerated when the temperature makes the ashes begin to melt and get pastry. The growing of the agglomerates will cause the de-fluidization of the bed. To avoid this, a more frequent exchange of the sand bed is required or the addition of inert mineral powders minimizing the contact with sticky particles, as dolomite or calcite.

Figure 20 Fluidized bed gasifier [35]



The syngas outlet temperature in fluidized bed gasifiers is usually within 700-900°C (except the HTW where the raw syngas temperature is increased by 150 to 200°C). It is free of tars and with low flying ash content. Suitable coals for this gasifiers are lignites and brown coals because of their higher ash content. Higher rank coals can operate in agglomerated ash gasifiers. Part of the H₂S and COS can be retained by the bed (up to 90%) with sorbents as limestone. This reduce as well the corrosion.

Depending on the sand bed movement three technologies can be distinguished: Bubbling Fluidized Bed Gasifier (BFBG), Circulating Fluidized Bed gasifier (CFBG) and Transport gasifier

	BFBG	CFBG	TRANSPORT
Gasification agent	Air/O ₂ /Steam/Mix	Air/O ₂ /Steam/Mix	Air/O ₂ /Steam/Mix
Operating temperatures(°C)	650-950	800-1000	800-1000
Operating pressure (bar)	1-35	1-19	11-18

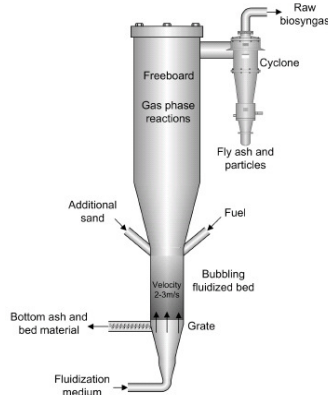


Figure 21 Bubbling bed gasifier [36]

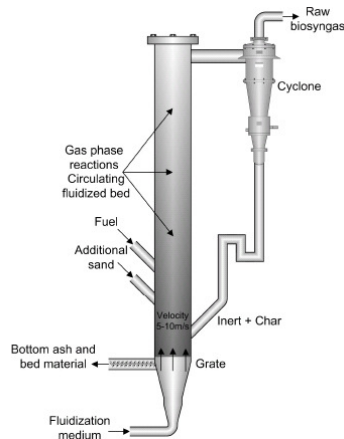


Figure 22 Circulating bed gasifier [36]

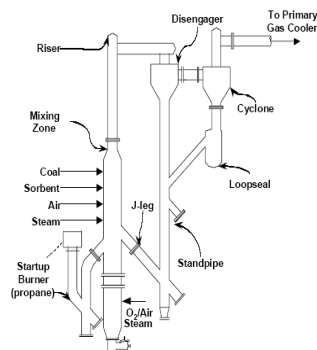


Figure 23 Transport reactor [37]

Table 16 Moving bed gasifiers by bed movement

BUBBLING FLUIDIZED BED GASIFIER (BFBG):

Oxidation agent is fed under the bed and this ascendant flow creates bubbles while traversing the bed. Fuel is fed into or above the sand bed. A cyclone at the exit of the syngas separates the fly ash. It is particularly useful for high ash coals, and/or those with variable characteristics

The main advantage of this gasifier is the higher carbon conversion rate compared with fixed bed gasifiers and, consequently, the high yields. Tar content in the product gas is quite low and the bed allows the use of catalysts.

Main disadvantages are the particulates content of the syngas and the risk of defluidization of the bed caused by the ash agglomeration. [36]

CIRCULATING FLUIDIZED BED GASIFIER (CFBG):

The velocity of the gasifying agent is faster than in the former case, to suspend the particles throughout the reactor.

A cyclone separates the particles (sand, char, fly ash) and recycles it into the bed.

Its advantages are the low tar content in the gas and its flexibility to calorific value and moisture of the fuel and to the particles size.

Main disadvantages are the particulates content of the syngas and ash agglomeration risk, as well as the erosion caused by high velocities of the gas. The heat exchange is less efficient than BFBG [36]

TRANSPORT REACTOR

This type is between fluidized bed and entrained flow gasifier. Higher air circulation velocities lead to a better mixing and heat transfer rates.

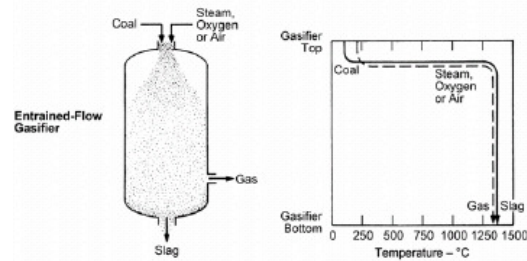
Limestone is usually added as sulphur sorbent, which reduces the need of a hot gas cleaning unit. The mixing section has a combustion zone and a coal devolatilization zone. The combustion zone is fed with recycled char, ash and sorbent and mixed with the oxidant and steam. Heat for the coal devolatilization and gasification reactions is afforded by the char combustion. The fresh coal and sorbent are injected above the combustion zone and are rapidly heated by the circulating solids and combustion gases in a devolatilization zone.

Additional residence time in the riser section allows the char gasification, methane/steam reforming, water gas shift and sulphur capture reactions to occur. After traversing the riser, primary and secondary cyclones separates the solids from the gas into a standpipe system connected with the mixing section. The exiting fuel stream from the secondary cyclone is sent through a raw gas cooler.

ENTRAINED FLOW GASIFIERS

Entrained flow gasifiers are characterized by higher velocities and higher temperatures than fixed or fluidized bed gasifiers.

Figure 24 Entrained flow gasifier [35]



Fuel has to be fed in small particles (200-300 μ m). The gasification agent flows co-currently with the fuel inside the gasifier and reach temperatures above the ash fusion temperature. The residence time is short (0.5-5 sec) The produced gas is free of tars and phenols and contains small amounts of methane.

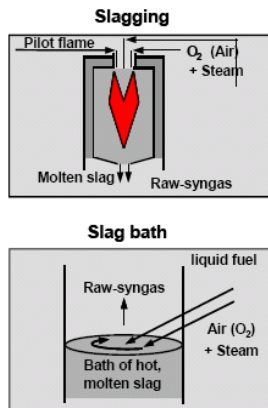
In principle, operating temperature should be higher than the AFT, but in order to ensure a safe operation, the operating temperature must be kept over the *Temperature of Critical Viscosity (TCV)* when slag begins to crystallize. The TCV depends on the slag composition ($\text{SiO}_2/\text{Al}_2\text{O}_3$)

Attending the gas flow movement two types of entrained flow gasifier can be distinguished:

	Down-flow	Up-flow
Gasification agent	Air/ O_2 /Steam/Mix	Air/ O_2 /Steam/Mix
Operating temperatures($^{\circ}\text{C}$)	1200-1600	1200-1600
Operating pressure (bar)	20-50	20-80

Table 17 Entrained flow gasifiers by syngas movement

Entrained flow



DOWN-FLOW GASIFIER: Coal is fed dry or with water by the top of the reactor. Gasification occurs at high temperatures and moderate pressures. The gas flows downwards and it is cooled or quenched with water at the bottom of the reactor. The slag drops into a water pool.

UP-FLOW GASIFIER: Fuel is fed by the bottom of the gasifier. Gas flows upwards and leaves the gasifier by the top part while the slag flows down and is quenched with water. This type of gasification can happen in one or two stage. When a two stage gasifier is used, the 75% of the coal is fed by the bottom part and the rest is directly injected into the hot gas in order to take advantage of its high temperature. Some char and hydrocarbons are produced in this second stage [35].

Figure 25 Down and up flow gasifiers

	FIXED or MOVING BED		FLUIDIZED BED			ENTRAINED FLOW
Operating Temperature (°C)	300-1100		650-1100			1500-1900
Operating Pressure (bar)	10-100		10-40			25-80
Product gas	Contains tar and oil, phenols, ammonia and small amounts of dust		Low tars and phenols. Uniform composition. High content of ash and char.			No tars and phenols but ash, char. Sensible heat must be recovered for higher efficiency
Gas outlet temperature (°C)	400-600		700-900			900-1600
Residence time (s)	900-3600		5-100			1-10
Feed coal type and size (mm)	Caking coals requires agitation of the bed (moving bed) 5-80		Caking coals require pre-treatment. Indicated for high ash coals 0.5-5			All types (low ash and easy to pulverize) <500 microns
Ash removal	Dry	Slagging	Dry	Agglomerating		Slagging
Coal rank	Low	High	Low	Any		Any
Oxidant requirement	Low	Low	Moderate	Moderate		Low
Steam requirement	High	Low	Moderate	Moderate		Low
Capacity (MWh)	Up-draft	Down-draft	Stationary	Circulating	Transport	100-1000
	0.25-2	0.25-2	2-20	15-100 3-300 (pressurized)	3-300	
Advantages	Small scale. Mature for heat. Can handle moisture. Non carbon ash	Small scale Low particles and tar.	Large scale. Direct or indirect heating	Large scale.	High carbon conversion. Large scale	Can be scaled Potential for low tar.
Disadvantages	Scale limitations High tar yield Feed size limits. Slagging risk.	Scale limitations Feed size limits. Moisture sensitivity	Medium tar yield Higher particle loading.	Medium tar yield Higher particle loading.		High particles content in the gas. Potentially high S/C

Table 18 Gasifiers Main characteristics and operating conditions[38][39]

1.2. Commercial technologies

ENTRAINED FLOW

TEXACO: single stage, downward firing gasifier in which a coal/water slurry (60 -70% coal) and 95% pure oxygen are fed at the top of the gasifier. Operating pressure for IGCC use to be around 20-30 bar but the pressure can be increased up to 80bar if necessary (i.e. in chemical industry). The hot syngas temperature ranges between 1260°C and 1500°C and it is further cooled to about 700 °C. There are two options for cooling the gas either quenching it with water or using a syngas radiant cooler. The first option minimizes cost while the second one optimizes the efficiency.

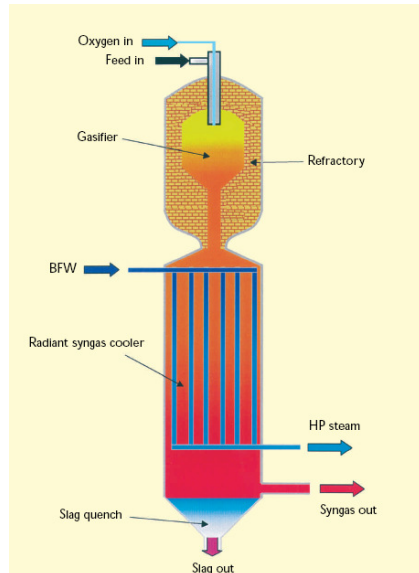


Figure 26 Texaco radiant cooler [40]

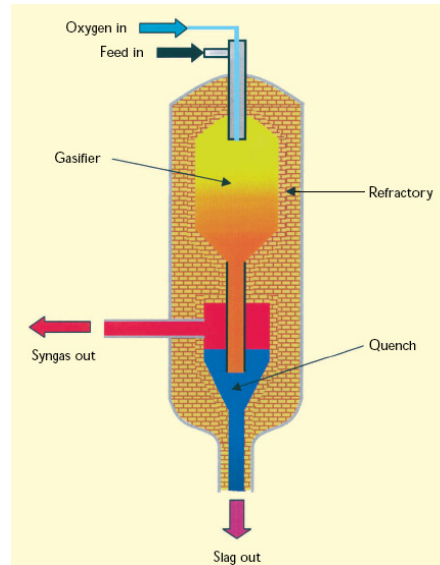
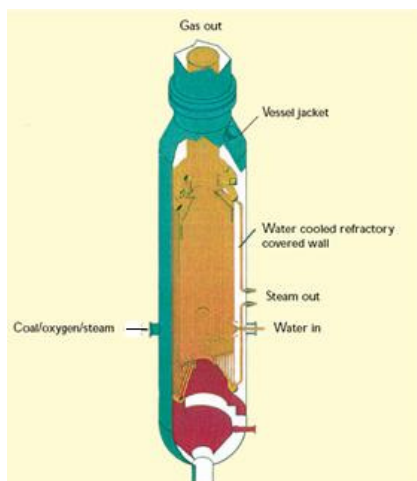


Figure 27 Texaco water quench [40]

SHELL: single stage, membrane walled, upward flow gasifier .



The coal is pressurized and dry fed at the bottom of the gasifier together with the oxygen. Operating pressure for IGCC use to be around 25-40bar but the pressure can be increased up to 65bar. The water circulating in the membrane wall helps to keep the temperature at the same time while producing medium pressure steam. The hot syngas leaves the reactor at a temperature between 1360°C and 1650°C. Clean product gas is then recycled and mixed with the hot gas in order to reduce the temperature to 900°C. Afterwards the gas traverses a cooler where high and medium pressure steam is generated. Part of the slag coats the membrane wall in order to minimize the heating losses through the wall. Prentice gasifier is similar to Shell gasifier.

Figure 28 Shell Gasifier [40]

MHI: air blown gasifier with two stages and upward flow. Dry pulverized coal is fed with air into the first stage and alone into the second. The exothermic reactions occurring in the combustors allow the reduction reactions during the second stage. The membrane water wall is covered by a layer of molten ash to minimize the heat loss. The syngas outlet temperature is not as high as for one stage gasifiers. After leaving the gasifier the syngas traverses a syngas cooler where its temperature decreases to 450°C. Afterwards the remaining char in the gas is separated in a cyclone and a porous filter to be recycled to the first stage[41].

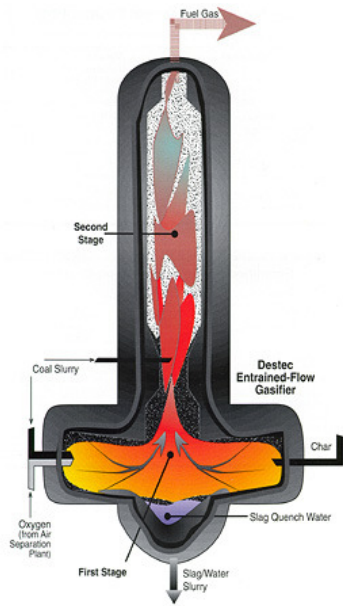


Figure 29 Conoco-Phillips gasifier [42]

SIEMENS: oxygen-blown dry feed gasifier with water quench and single stage. Gasification temperature is between 1400-1600°C. Low pressure steam is generated in the water circulating membrane wall. After leaving the gasifier, the gas is quenched with water to about 230°C

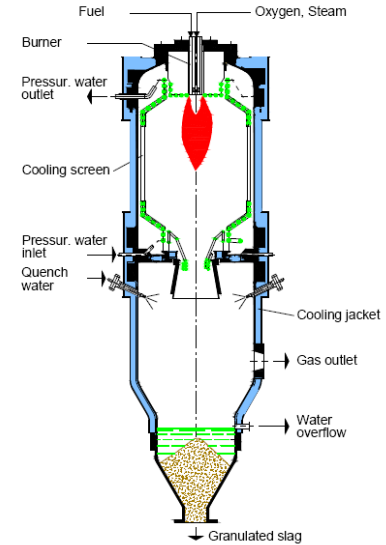


Figure 30 Siemens gasifier

TECHNOLOGY	COAL FEED	FLOW	STAGES	SYNGAS COOLING	OXYDANT
TEXACO	WATER SLURRY	DOWN	1	WATER QUENCH OR COOLING	AIR/O ₂
SHELL SCGP	DRY	UP	1	GAS QUENCH AND COOLING	AIR/O ₂
PRENFLO	DRY	UP	1	GAS QUENCH AND COOLING	O ₂
MHI	DRY	UP	2	COOLING	AIR
ABB-CE	DRY	UP	2		AIR
HITACHI	DRY	UP	2		O ₂
Conoco-Phillips-E-Gas (Destec)	WATER SLURRY	UP	2	COOLING	O ₂
Siemens (Future Energy; NOELL/GSP ;BBP)	DRY	DOWN	1	WATER QUENCH	O ₂

Table 19 Commercial entrained flow gasifiers

TECHNOLOGY	P (bar)	T (°C)	Ash type	Wall
TEXACO	20-80	1204-1500	Slag	Refractory
SHELL SCGP	24-65	1500-1600	Slag	Membrane
PRENFLO	>25	1200-1600	Slag	Membrane
MHI	>25	1200-1500	Slag	Membrane
Conoco-Phillips-E-Gas (Destec)	>27	1400	Slag	Refractory
Siemens (Future Energy; NOELL/GSP ;BBP	5-26	1400-1600	Slag	Membrane

Table 20 Commercial entrained flow gasifiers

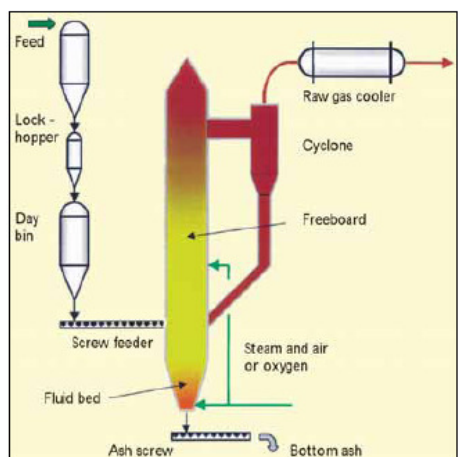
Raw gas comp (dry)	H ₂	CO	CO ₂	CH ₄	COS	H ₂ S	NH ₃	N ₂ +Ar	CGE	REF
Technology	%vol	%vol	%vol	%vol	%vol	%vol	%vol	%vol	% HHV	
TEXACO	36.28	47.42	12.93	0.12	0.024	1.2	0.2	1.92	75.5	[28] [45]
SHELL	27.24	64.36	1.53	0.03	0.1	1.33	0.02	5.3	79.6	[28] [45]
PRENFLO	26.74	62.13	1.32	0.01	0.11	1.01	0	8.65	82.47	[43]
DESTEC	37.6	50.35	9.95	-	-	-	-	1.05	75	[44] [45]

Table 21 Commercial entrained flow gasifiers for a coal Illinois #6

CGE=Cold Gas Efficiency

FLUIDIZED BED

MBEL: air-blown spouted/fluidised bed, designed to operate without ash agglomeration. Only the 70% - 80% of the coal is gasified. The addition of sorbents such as limestone or dolomite allows the gasification of coals with high sulphur content. Char and solid residues can be burned in a separated boiler to generate steam. The generated gas has a low heating value (around 3.6MJ/m³) Total efficiency is around 46-48%



HTW: Coal is dry fed at the bottom of the gasifier together with the air or oxygen. The temperature is kept under the AFT and the operating pressure can go from 10 to 30bar. Particles are removed in a cyclone and fed back to the gasifier. The gas is cooled from 900°C to 300°C in a syngas cooler where steam is generated.

Figure 31 HTW Gasifier [40]

KRW: Agglomerating fluidized bed gasifier. Coal is fed at the bottom of the gasifier with or without limestone injection for sulphur capture. Raw gas leaves the gasifier at around 1000°C and it traverses a cyclone where trained particles are removed and recycled into the gasifier. The gas is further cooled to 540°C in a syngas cooler. A stream of recycled gas is injected at the bottom of the gasifier in order to cool the char, ash and spent sorbent.

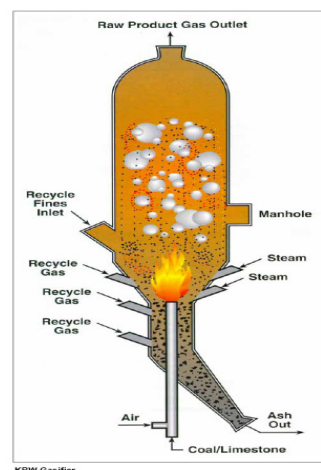


Figure 32 KRW gasifier [40]

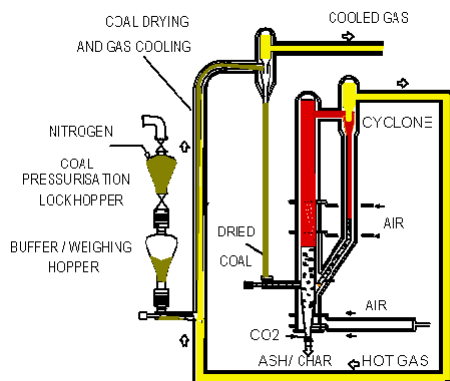


Figure 33 IDGCC gasifier [46]

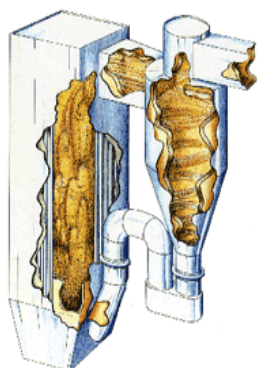


Figure 34 Lurgi CFB gasifier [47]

IDGCC (Integrated Drying Gasification Combined Cycle) : The particularity of this air-blown gasifier is that the coal is dried under pressure using the heat in the gas leaving the gasifier. The gasifier operates at a temperature of around 950°C and 25 bar of pressure. The cooled gas leaves the coal drier at a temperature of about 250°C. Fines and particles are removed in a ceramic candle barrier.

LURGI CFB: The circulating fluidized bed of the gasifier favors the heat and mass transfer. Operating temperatures goes from 850°C to 900°C. The gas entrains a considerable portion of the solids that are separated from the gas in one or more recycling cyclones located downstream of the combustor, and are continuously returned to the bed by a recycle loop. Combustion air is fed to the combustor at two levels. About 40% of the combustion air is introduced as primary or fluidizing air through the grate at the bottom, and the balance is admitted as secondary air through multiple ports in the side walls. Coal combustion thus takes place in two zones: a primary reducing zone in the lower section of the combustor followed by complete combustion using excess secondary air in the upper section

KBR: It consists of two sections: a short, larger-diameter mixing zone and a longer, smaller-diameter riser. Air and steam are introduced at the bottom of the mixing zone to raise heat by burning the carbon in recirculated char. Coal and sorbent are fed to the top of the mixing zone to separate the coal from the oxidant and avoid burning volatile material produced when the coal is heated. All of the solids and gases are carried from the mixing zone into the riser where devolatilization and carbon-steam gasification reactions occur. In addition, some of the sulfur released from the coal is captured as calcium sulfide by the calcium in the coal and added calcium-based sorbent. The majority of the unreacted char and sorbent-derived material leaving the riser is captured by a disengager and cyclone assembly and recycled back to the mixing zone through a standpipe and a nonmechanical “J-valve.” The synthesis gas and fine char that is not captured in the cyclone are cooled in a heat exchanger before entering a metallic candle-filter particulate collection device, which removes any remaining particulate matter from the gas [48]. Gasification temperatures are between 815°C and 1065 °C and the pressure can vary from 9.5 to 18bar.

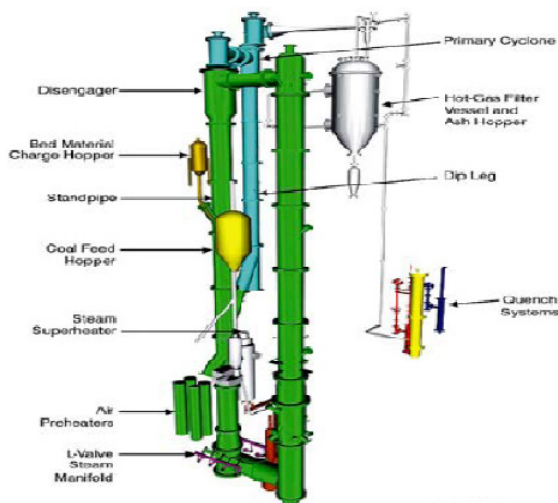
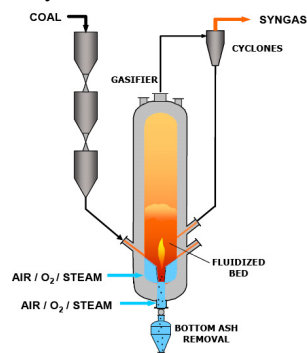


Figure 35 KBR gasifier [28]



U-GAS (IGT): Coal is pneumatically fed through a lockhopper system. Gasification temperatures ranges from 950 °C to 1100°C. Nevertheless the temperature is controlled to maintain nonslagging conditions for ash. The operating pressure utilized depends on the ultimate use of product gas and may be varied, as required, between 3.5 and 31bar.

Figure 36 U-gas Gasifier [28]

TECHNOLOGY	COAL FEED TYPE	OXYDANT	BED TYPE
MBEL (ABGC)	DRY	AIR	BUBBLING
HTW	DRY	AIR/ O ₂	BUBBLING
KRW	DRY	AIR/ O ₂	BUBBLING
IDGCC	DRY	AIR	BUBBLING
U-GAS (IGT)	DRY	AIR/ O ₂	BUBBLING
Lurgi CFB	DRY	AIR/ O ₂	CIRCULATING
KBR	DRY	AIR/ O ₂	TRANSPORT

Table 22 Fluidized bed gasifiers

TECHNOLOGY	P (bar)	T (°C)	Ash type	Wall
MBEL (ABGC)	20-25	1000	Dry	Refractory
HTW	10-30	800-1100	Dry	Refractory
KRW	20-30	870-1040	Agglomerate	
IDGCC	20-30	800-1000	Dry	
U-GAS (IGT)	3.5-31	950-1100	Agglomerate	
Lurgi CFB	Atmospheric	800-950	Dry	Refractory
KBR	9.5-18	815-1065	Dry	Refractory

Table 23 Fluidized bed gasifiers

MOVING OR FIXED BED

BHEL: A mixture of air and steam is used as a gasificiant agent. After leaving the gasifier the gas is cooled in a syngas cooler where tar deposition can cause a loss of performance. After cooling, the gas is quenched with water in order to condensate the tars. Particulates are removed with a Venturi scrubber.

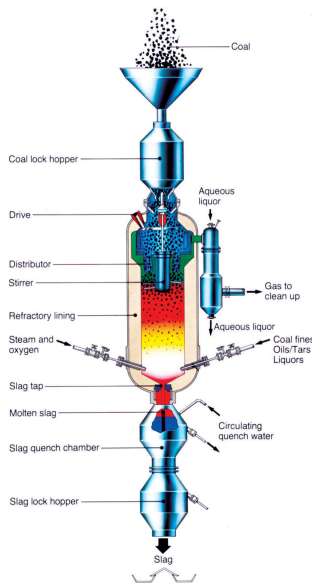


Figure 37 BGL gasifier [49]

The gas leaves the reactor at 540°C and is further quenched with water to condense the tar. The ash is removed by a rotating grate placed at the bottom of the gasifier and discharged via an ash lock pressurized with steam

BGL: Coal is introduced into the pressurised gasifier through a lock-hopper at the top of the vessel. Coal moves down opposite to the rising gas and undergoes pyrolysis, gasification and combustion reactions. Oxygen and steam are injected through tuyeres into the combustion zone where remaining char is combusted.

The temperatures in the reactor are high enough to melt the ash. Liquid slag flows down the gasifier and is discharged into a water quench.

The gas leaves the gasifier to around 500°C and it is quenched with water. Soluble compounds that are removed at this stage from the gas together with the entrained particles, are further separated from the aqueous liquor and reinjected into the gasifier.

Lurgi: Coal is fed in the top section of the reactor through a lock-hopper and moves downward countercurrent to the flowing gas. Operating pressure is around 30 bar and the temperature can reach the 1100°C. The reactor is cooled by water circulating in the space between the double wall of the vessel at the same pressure than the gasifier.

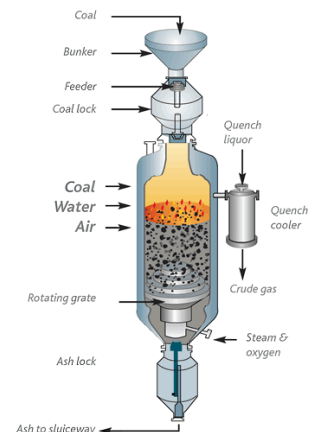


Figure 38 Lurgi gasifier
Source: Sasol

TECHNOLOGY	COAL FEED TYPE	OXYDANT	ASH TYPE	T (°C)	P (bar)
BHEL	DRY	AIR	DRY	1000	11
LURGI	DRY	AIR/ O ₂	DRY	1100	<=85
BGL	DRY	O ₂	SLAG	1000	30

Table 24 Fix bed gasifiers

1.3. Matching gasifiers to coals

Gasifiers efficiency and stability is ensured under a range of values of certain characteristics of the coal. These properties have to be considered for the gasifier selection in order to ensure the quality of the produced gas.

In order to select most appropriate reactor for each coal the next coal characteristics have to be considered:

1. *Coal moisture content*: the energy value of the produced gas depends in part on the moisture content of the fuel. The control of moisture in the feedstock is critical for an efficient gasification. Besides, it can determine whether the coal feed into the gasifier must be dry or slurry.
2. *Volatile matter of the fuel*: Determines the extent and rate of gasification reactions. Affects to the generation capacity
3. *Ash content*: Decreases the system efficiency and increases the slag production and disposal cost. It can cause slagging or clinker formation in the reaction due to the melting and agglomeration of the ashes. Slagging can end up in excess of tar formation that can block the reactor, mainly in fixed bed gasifiers. It can occasion pressure drops and air channelling which can cause variable product gas temperatures and composition and, in worst case, a downstream explosion.

To avoid slagging , fuel ash content must be below 6%. Above the 12% there is a high risk. Between 6% and 12% ash fusion temperature and ash composition determine the slagging behaviour. [50]

Moving bed gasifiers (with bed stirring) can tolerate slagging and entrained flow gasifiers are all slagging. Membrane walled EFG use a slag self-coating to minimize heat losses through the wall. Therefore, besides the maximum ash limit tolerance (based on technical and economical reasons) , there is a minimum ash content on the fuel required for the self-coating of the reactor walls that depends on the technology: Sekk (>8 wt %), the BBP and the Hitachi (>1 wt %).

4. *Ash compounds*: Certain substances contained in the ash (CaO, SiO₂, Fe₂O₃ ...) can attack the refractory material and give rise to cracks [51]

Sodium compounds (NaCl or NaOH) and other alkali matter diffuse into the refractory lining of the reactor which leads in turn to a gradual disintegration and loss of life of the refractory[30]. Besides, in up-flow gasifiers where the gas is cooled and not water quenched, alkaline compounds can evaporate and leave the gasifier together with the gas, adhering later on the pipes walls. The control of the operating temperature is compulsory for coals with high alkali content

Agglomeration is another ash-derived problem that can affect the process. The presence of Fe₂O₃, SO₃ and sodium silicates formed during gasification can cause agglomeration.

5. *Ash fusion temperatures(AFT), temperature of critical viscosity (TCV), softening temperature(ST)*:

During the slag cooling, if the temperature of critical viscosity (TCV) is reached, the formation of solids (crystals) makes the fluid behave as a non-Newtonian fluid, increasing the apparent viscosity of the slag.

Softening temperature (ST) is considered as the temperature where agglomeration starts.

Depending on the ash disposal characteristics of the gasifier, operating temperature should be above or not the ash fusion temperature

- Dry ash: Operational temperature must be always higher than the AFT
- Slagging: Operating temperature must be over AFT In slagging gasifiers the slag should be removed at a temperature above the TCV in order to avoid the effect of crystals. The slag viscosity has to be lower enough to allow the slag flow between bed particles. The fusibility of the ash has been reported to be a function of the content of the eight principal oxides frequently found in coal ash: the glass formers (SiO₂, Al₂O₃, TiO₂) and the fluxing agents (Fe₂O₃, CaO, MgO, Na₂O and K₂O) . The acid/base ratio is the most frequently used parameter for correlating ash fusibility with its composition.
- Agglomerate: Operating temperature must be over the softening temperature and below the fluid temperature.

6. *Other compounds*

- Sulphur: May cause corrosion of heat exchanger surfaces. In most of the cases the solution is to avoid high temperatures rather than lower the sulphur content of the fuel [30] The use of solvents in the fluidized bed allows the use of coals with higher sulphur content.
- Chlorine: Formation of HCl which is a reactive, corrosive, and toxic gas that can cause corrosion

7. *Char reactivity* : A measure of the rate at which residual char from a given coal will react with CO₂ under arbitrary and fixed conditions of temperature and gas composition. It affects the combustion efficiency, the ability of fuels to create NO_x, the temperature distribution in the furnace etc Reactivity dictates the dimensions of reduction zone that are required and the residence time required for complete gasification. Coals with low char yield and high char reactivity (as lignites or brown coals) mainly for fluidized bed gasifiers. However, those working with slagging ash can operate with higher rank coals.

The reactivity decreases with coal rank and increases with the oxygen functional groups content of the fuel.

8. *Grindability*: Indicates the ease of pulverizing a coal in comparison to a reference coal. This index is helpful in estimating mill capacity. Two factors affecting grindability are the moisture and ash contents of a coal. coal. The The Hardgrove Grindability Index (HGI) measures how ease is to pulverize a coal in comparison with a standard coal with an assigned HGI value of 100 grindability. The higher the grindability index, the easier the coal is to grind. In general, coals with a low index (lignites and anthracites) are more resistant to grinding than are bituminous. Coals with high HGI are more suitable for slurry feed gasifiers. Fluidized bed gasifiers use only crushed fuels (except transport reactor)
9. *Bulk density*: Bulk density is defined as the weight per unit volume of loosely tipped fuel. A high bulk density means a high energy-for-volume value. The reactor dimensions are more reduced for a given refuelling time. Low bulk density fuels sometimes give rise to insufficient flow under gravity, resulting in low gas heating values and ultimately in burning of the char in the reduction zone [50].

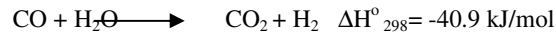
This table gather the reference value for most of the explained parameters, based on the type of gasifier:

PARAMETER	FIXED BED	FLUIDIZED BED	ENTRAINED FLOW
Moisture	<ul style="list-style-type: none"> • Dry feed: 2% • Slurry feed: 10% Counter-current gasifier is more tolerant.	<55%	Can handle a wide range of moisture content.
Volatile matter	A wide range is used	A wide range is used	A wide range is used
Ash content	<15%	<40%	<25% >1% or >8% (depends on the technology)
Ash compounds	Low Fe ₂ O ₃ , SO ₃ and sodium silicates Low alkali compounds	Low alkali compounds	Low alkali compounds in up-flown gasifiers and refractory lined
Ash fusion temperature	<ul style="list-style-type: none"> • Dry ash: T< AFT • Slagging T> AFT 300°C<T<1000 °C	T<AFT AFT>1100 °C	T>AFT AFT<1500 °C
Sulphur and Chlorine	S<1.5% Cl<0.4%	S<1.5% Cl<0.4%	S<1.5% Cl<0.4%
Char reactivity	<ul style="list-style-type: none"> • Dry: High reactivity chars to allow carbon conversion at low temperatures • Slagging: A range of reactivity can be used because of the high operational temperature (T) 	High reactivity chars to allow carbon conversion at low temperatures	A range of reactivity can be used because of the high operational temperature (T)
Grindability	Low (except if slurry feed)	Medium	High

Table 25 Matching coals to gasifiers [52]

C.2. WATER GAS SHIFT REACTION (WGS)

WGS is the chemical process in which carbon monoxide reacts with water to produce carbon dioxide, hydrogen and heat.



As the reaction is equimolar it does not depend on pressure and lower temperature can favour higher conversion but requires more catalyst. Usual reaction temperatures vary from 200°C to 500°C depending on the quality and operational temperature of the catalyst.

The gasification syngas can be shifted after or before desulphurization. The processes are then referred to as clean or sour gas shift.

Parallel reactions as methane steam reforming and COS hydrolysis occur in the shift reactor. To afford the necessary water to the reactor, the gas is prior saturated regarding a steam/C ratio around 2, to avoid carbon depositions in the reactor.

2.1. Clean Gas Shift

In order to minimize the kinetic limitations of the process due to low temperatures and maximize the hydrogen production, the reaction is normally carried out in two stages, one at high temperature and other at low. The catalysts used are different for each case.

HIGH TEMPERATURE SHIFT :

Iron oxide based catalyst is used in this process at temperatures ranging from 300 °C to 500 °C. In order to control catalyst temperature, two intercooled reactors can be used. The first one reduces CO to a 7-8%mol level, and on the second one the final concentration reaches the 3.2%mol. During the cooling of the shifted gas, high sulphur concentrations (>100ppm) have to be avoided to keep catalyst undamaged.

LOW TEMPERATURE SHIFT :

Operating temperatures of the used copper-zinc-aluminium catalyst range from 200 °C to 270 °C. Final CO levels are reduced to around 0.3%mol.

The catalyst does not tolerate a H₂S concentration and even 0.1 ppmv in the inlet gas can damage the catalyst over the time. Besides, condensation in the reactor has to be avoided[30].

2.2. Raw Gas Shift

A sulphur tolerant cobalt-molybdenum catalyst is used. Operating temperature is around 250 °C. The use of two or three intercooled adiabatic reactors results in a final CO concentration of 1.6 to 0.8%mol.

Side reactions are the hydrolysis of the COS contained in the feed gas as well as the hydrogenation of HCN and unsaturated hydrocarbons. Sulfides deposition due to the carbonyls decomposition increases the pressure drop of the reactor [30].

Performance Criteria	Units	Low/Medium Temperature Shift	High Temperature Shift	Sour Gas Shift
Catalyst Form	-	pellets	pellets	pellets
Active Metals	-	Cu/Zn & Cu/Zn/Al	Fe/Cr	Co/Mo
Reactor Type	-	multiple fixed beds (last bed)	multiple fixed beds	multiple fixed beds
Temperature ^a	°C	200-270/300	300-500	250-550
Pressure	psia	~450	450-750	~1100
CO in Feed	-	low	moderate to high	high
Residual CO	%	0.1-0.3	3.2-8	0.8-1.6
Approach to Equilibrium	°C	8-10	8-10	8-10
Min Steam/CO Ratio	molar	2.6	2.8	2.8
Sulfur Tolerance	ppmv	<0.1	<100	high ^b
COS Conversion	-	no	no	high
Chloride Tolerance	-	low	moderate	moderate
Water Tolerance	-	low	moderate	high
Stability/Durability	years	3-5	5-7	2-7

Table 26 Performance of commercial WGS [53]

^a Lower temperature limit is set by water dew point at pressure.

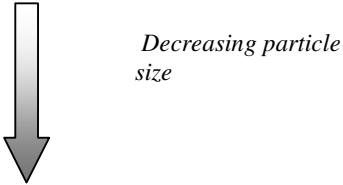
^b Sulfur is required in the feed gas to maintain catalyst activity.

C.3. Cold/Warm gas cleanup

3.1. Particulate removal

To avoid downstream erosion problems, dust has to be removed from the gas. This can be done applying external forces or passing the gas through a barrier system.

Main particle removal methods are shown in the following table:

	Based on external forces	Based on barriers	
	Gravity settlers	Granular bed filters* Bag filters Rigid barrier*	FILTERS
	Cyclones and centrifuges	Wet scrubbers	
	Electrostatic precipitators		

* Explained in the hot gas particulate removal section

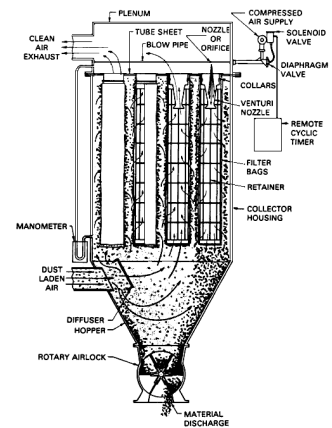
Table 27 Particulate removal from cold gas [54]

METHODS BASED ON BARRIERS

FABRIC FILTERS

Usually referred to as baghouses, they consist on a group of many bags hanging vertically in a support. Each bag is made of a filter medium that retains the particulate while the gas traverses through the cloth. The dust is removed from the bag surface by reverse air cleaning, by shaking/deflating the bag or via a pulse jet system.

Figure 39 Fabric filter [55]



This last method allows the cleaning of some bags without interruption of the operation of the rest of the bags.

Depending on the design, the gas flows from the interior of the bag to the exterior or in opposite direction.

Main failure causes of baghouses are caused by abrasion, high temperature or chemical attack. Abrasion can be caused by the bags rubbing against each other or by the cleaning system use that can deteriorate the bag at the attachment point

Temperature has to be controlled given that high temperatures can affect the fabric material but, on the other hand, low temperatures can produce moisture or acids condensation on the bag. The fabric material should be selected according to operating temperatures[56].

FIBRE	Generic name	Aramid	Glass	PTFE	Polyphenylene sulphide	Polybenzimidazole
	Trade name	Nomex	Fibreglass	Teflon	Ryton	PBI
	Recommended continuous operation temperature (°C) dry heat	204	260	260	190	260
	Water vapour saturated condition (moist heat) (°C)	177	260	260	190	260
	Maximum(short time)operation temperature (dry heat) (°C)	232	290	290	232	343
	Relative moisture regain in % (in 20°C and 65% relative moisture)	4.5	0	0	0.6	14
	Resistance to alkalis	Good	Fair	Excellent	Excellent	Good
	Resistance to mineral acids	Fair	Very good	Excellent	Excellent	Excellent
	Resistance to organic acids	Fair	Very good	Excellent	Excellent	Excellent
	Resistance to oxidising agents	Poor	Excellent	Excellent	Attacked by strong oxidising agents	Fair
	Resistance to organic solvents	Very good	Very good	Excellent	Excellent	Excellent

Table 28 Fabric filter materials [54]

Highest removal efficiencies are reached for large particles at high gas velocities. Average pressure drop of the gas is around 0.01-0.015 bar

Removal efficiency 98-99.9%
Particle size range 0.01- 100 μm

WET SCRUBBER

Particulates, as well as trace quantities of chlorides and ammonia are removed from the synthesis gas putting it in close contact with fine water drops. Wet scrubbers work at temperatures below the dew point.

Removal efficiency 90-99.9%
Particle size range 0.5 - 100 μm

There are three types of wet scrubber:

- Packed Bed:* Is the most used scrubber. When the gas pass through the packed structure, it gets in contact with the scrubbing liquor and the contaminant is absorbed into or reacted with it.
- Fluidised Bed Scrubbing:* There are two or more beds of low density spheres in the tower,. These spheres are fluidized by the gas stream between upper and lower retaining grids. The residence times are very short.
- Venturi Scrubber:* Used for particulates removal from gas streams. It is very efficient even down to sub-micron size. Venturi scrubbers efficiencies range from 70 to greater than 99%. Collection efficiencies are generally higher for particulates with aerodynamic diameters of approximately 0.5 to 5 μm

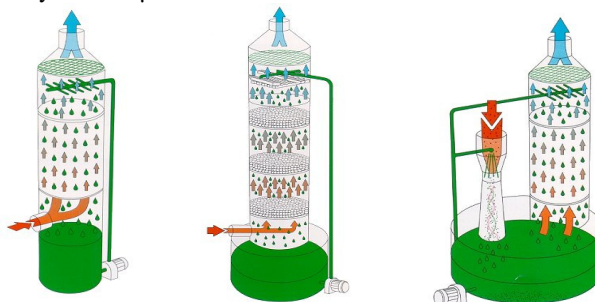


Figure 40 Packed bed, fluidised bed and Venturi scrubbers [57]

METHODS BASED ON EXTERNAL FORCES

GRAVITY SETTLERS

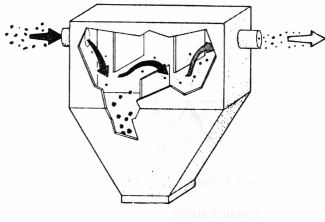


Figure 41 Gravity Settler [54]

They are also referred as gravity collectors, expansion chambers or outfall chambers. A gravity settler consists of an enlargement of the duct where the gas is slow down and particles fall down into the dust collecting hoppers. When the gas flow reaches the laminar regime, particulate removal becomes more efficient. Pollutant load can range from 20 to 4500 gr/m³.

The use of thermal insulation can avoid condensation which can cause corrosion, dust build-up and plugging of the hopper or dust removal system.

Particle size range > 50µm-1 mm

CYCLONES

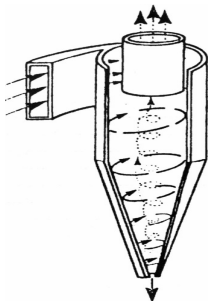


Figure 42 Cyclone [54]

Dust is mechanically removed from the gas thanks to the swirling movement that induces on the particles high tangential forces. Thus, particles flow downwards and leave the cyclone by the bottom outlet while the gas turns upwards. The pressure drop of the gas is around 0.01 bar. Reasonable efficiencies can be reached using two or three cyclones in series.

Cyclone efficiency generally increases with particle size and/or density, inlet duct velocity, cyclone body length, number of gas revolutions in the cyclone, ratio of cyclone body diameter to gas exit diameter, dust loading, and smoothness of the cyclone inner wall. A common factor contributing to decreased control efficiencies in cyclones is leakage of air into the dust outlet.

Typical flow rates of a single cyclone are 0.5-12 m³ with a pollutant loading from 2.3 to 230 gr/m³.

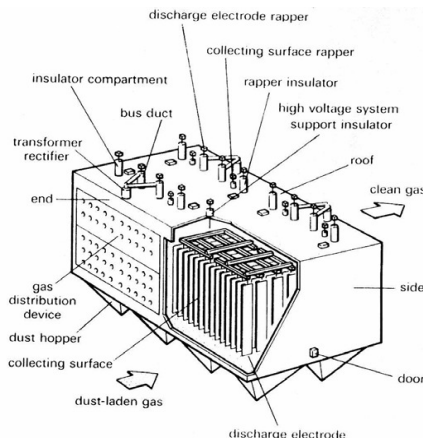
Particulate removal efficiency: 85-90%

Particle size range > 10 µm

Three types of cyclones can be differentiated:

1. *High efficiency cyclones:* designed to be effective for particles sizes over 20 µm (efficiency: 80-99%), 10 µm (efficiency: 60-95%) or over 2.5 µm (efficiency: 20-70%). It results in a higher pressure drop.
2. *Conventional cyclones:* It removes particles over 10 µm (efficiency: 50-90%).
3. *High throughput cyclones:* Removes particles over 20 µm with an efficiency of 80-99%. For particles of 10 µm, the efficiency will be under 40%.

ELECTROSTATIC PRECIPITATORS (ESP)



High efficiency, particulate removal device that collects particulate matter from gas streams. The electrostatic precipitator works by first charging the particulate matter entrained in the gas stream with high voltage discharge electrodes and then electrostatically influencing those particles to oppositely charged collecting plates within the ESP.

1. *Plate ESP:* Discharge electrodes are wires placed between two adjacent collection plates.
2. *Tubular ESP:* Discharge electrodes are located in the centre of the cylindrical collection electrodes.

Figure 43 Electrostatic Precipitator [54]

Typical flow rates are 100-500m³/sec with a pollutant loading going from 2 to 110g/m³.

Removal efficiency 98-99.9%

Particle size range 0.1 - 10 µm

3.2. Acid Gas Removal

Main sulphur compounds contained in coal gasification gas are COS and H₂S. Sulphur compounds are very corrosive and can poison clean gas shift catalyst or damage the gas turbine materials or the fuel cell anode.

In most of the cases to remove COS, it has to be previously hydrolyzed with water and a catalyst to H₂S and CO₂. Further removal of H₂S can be carried out following different processes. Most conventional technologies work at low temperatures and capture the H₂S thanks to chemical or physical solvents. More innovative methods use copper or calcium based solvents that can work at higher temperatures.

In general, the different methods for purification of the gas can be classified in:

- Chemical Absorption
- Chemical Adsorption (Chemisorption):
- Physical Absorption
- Physical Adsorption (Physisorption)
- Physical/chemical absorption

Chemical sorption involves a stronger bond between the species that may require more energy (i.e. steam) during the regeneration step. The most common use of physisorption processes is for bulk removal of carbon dioxide or selective H₂S removal. Sorbents for physisorption are expensive[54].

GAS DESULPHURIZATION

SOLVENT	REMOVAL MECHANISM	SOLVENT	NAME
CHEMICAL	AB	Potassium carbonate	Vacasulf Process
		Sodium carbonate and potassium carbonate	Vacuum carbonate
		Sodium carbonate	Seaboard
		Chelated iron solutions	Sulferox/ LO-CAT/ Sulfint
		Quinone and Vanadium metal	Stretford [*] Perox/ Takahax/ Hiperion /Sulfolin
	AD	Granular activated carbon(GAC) impregnated with alkaline or oxide coatings.	Impregnated activated carbon
		Iron oxide	Iron Sponge/Sulfa Treat/Sulfur-Rite

Table 29 Gas desulphurization methods

* liquid redox process
AB=Absorption
AD=Adsorption

❖ CHEMICAL ABSORPTION

VACASULF

Vacasulf is a process of desulphurization of ammonia-lean gases. H_2S is absorbed by a potassium carbonate solution in a low pressure scrubber (atmospheric pressure) followed by a high pressure scrubber (12 bar) and a sodium hydroxide scrubber [58] Its main characteristics are a high degree of desulphurisation and a relative low investment and operating costs. Besides, one of the products is high purity sulphur.

SEABOARD PROCESS

Seaboard process is a variation of the Vacuum Carbonate. It uses an absorbent solution containing 3.0 to 3.5 wt% of sodium carbonate.

The absorption reaction is: $2\text{H}_2\text{S} + 2\text{Na}_2\text{CO}_3 = \text{NaHCO}_3 + \text{NaHS}$

Sorbent regeneration is carried out by stripping the gas with 1.5 to 3 times more low pressure air than sour gas. Removal efficiencies can reach the 85% to 95% of the H_2S in the feed gas in a single stage. However, the presence of the H_2S in the foul air complicates its disposal. In addition, the oxygen contained in the air can produce side reactions during the absorbent regeneration, as the formation of NaSCN that causes disposal problems[58] [59].

As in the Vacuum carbonate process, trace amount of solvent in the gas may be harmful for the gas turbine.

SULFEROX PROCESS

It is an iron redox process where oxygen from the air oxidizes H_2S to water and sulfur, with the oxidation mediated by an iron chelate that is regenerated at 0.6 bar with air two or three times stoichiometric requirement. Sulphur may be recovered as a moist filter cake (around 80%wt H_2S) or as pure liquid sulphur (>99.5%wt).

The amount of circulating liquid is small. H_2S concentration in the clean gas can be as low as 5 ppmv. COS is slowly hydrolyzed to H_2S and a 30-60% is removed if the residence time is slowly enough. If the presence of ammonia is too high, pH increases and may cause iron precipitation.

Operating temperature goes from 20 °C to 40 °C. Pressure drops from 0.2 to 0.7 bar in the absorber[58].

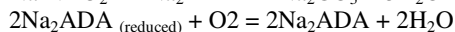
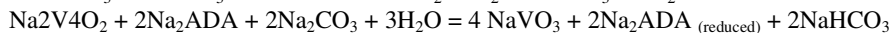
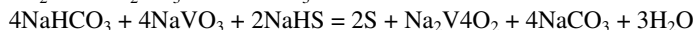
Another technology of similar characteristics is the LO-CAT process that uses ferric iron in a solution of organic chelating agents. This solution is not toxic and final H_2S removal efficiency is very high (up to 99.99%).

The Sulfint process uses EDTA as iron chelating agent. Main inconveniences of this method are the slow oxidation rate in the oxidizer and the low purity of the sulphur stream[60].

STRETFORD PROCESS

The process uses a solvent containing sodium carbonate, anthraquinone-disulfonic acid (ADA) and sodium metavanadate. These chemicals are stable, non-toxic and easily treated. H_2S can be reduced to 0.1 ppm.

Stretford process is based on the following reactions :



Operating temperature is around 30-40 °C while the pressure can vary from atmospheric pressure to 7 bar aprox. The presence of CO_2 in the gas decreases the H_2S absorption efficiency. COS is not absorbed for this process while ammonia reacts with solid sulphur to produce polysulfides [61]. Mercury has to be removed from the sour gas before entering into the desulphurization process to avoid the contamination of the final sulphur stream.

The main inconvenience of this process is that contains substances that may be harmful for the gas turbine. Even trace amount of solvent in the fuel has to be avoided. Besides, liquid waste streams containing alkalis, vanadium, ADA, $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2SO_4 may create disposal problems[58]

Other processes working with quinine and/or vanadium solvent and under analogue conditions are Perox, Takahax, Hiperion and Sulfolin [59][62].

Perox and Takahax processes profit of the redox potential of organic quinone solutions to convert hydrogen sulphide to elemental sulphur. The main disadvantage of the Takahax process is the long residence time required for the reoxidation of the absorbent.

Sulfolin employs organic nitrogen vanadium promoter instead of ADA, resulting in a lower rate of byproduct formation.

❖ *CHEMICAL ADSORPTION*

IMPREGNATED ACTIVATED CARBON

Granular activated carbon has a highly porous adsorptive surface. When the activated carbon is impregnated with alkaline or oxide solids (sodium or potassium hydroxide, sodium carbonate, potassium iodide or metal oxides), the selective adsorption of the H_2S is enhanced. H_2S load is about 20-25%wt and a final concentration of 0.2 ppm of H_2S can be reached.

Operating temperature is limited to 65.5°C for the adsorption and 260 °C for the regeneration [59].

IRON SPONGE

The H_2S is adsorbed by a bed of hydrated ferric oxide at a pressure around 5-25bar and a temperature between 25-50°C. High pressure operation is allowed up to 70bar. Residence time is greater than 60 sec. The inlet gas is saturated in order to keep the required moisture conditions in the vessel(around 40% moisture content)

The life of the bed can be extended by regeneration with atmospheric air but the it must be replaced before it gets fully loaded with sulphur . Final H_2S is reduced to ppm level[63].

Other methods using iron oxide adsorbents are SulfaTreat and Sulfur-Rite

SulfaTreat uses a Fe_2O_3 or Fe_3O_4 compound coated onto a granulated support commercialized by SulfaTreat Company. Acid gas load is around 0.55-0.72 kg H_2S /kg iron oxide[58]. The adsorbent is easier to handle than the iron sponge but it present the same inconveniences: non-regenerability and disposal problems.

Sulfur-Rite process utilizes an iron oxide product that increases the removal efficiency (3-5 times more efficient than iron sponge). The final product is insoluble iron pyrite[64]

COLD GAS DESULPHURIZATION/DECARBONISATION

The following methods allow the combined removal of H₂S and CO₂ when both are present in the gas stream. When selective methods are applied, separated streams of each contaminant can be obtained, which favours CO₂ disposal. Non selective methods can be used as well for CO₂ post-combustion capture when H₂S has been removed previous combustion by a different desulphurization process.

SOLVENT	REMOVAL MECHANISM	SELECTIVITY	SOLVENT	NAME
CHEMICAL	AB	NS	Sodium carbonate and potassium carbonate	Vacuum carbonate
			Sodium carbonate	Seaboard
			Hot potassium carbonate	Catacarb
			Hot potassium carbonate	Benfield
			Hot potassium carbonate	Giammarco-Vetrocoke
			MEA	MEA/Sulfiban
			DGA	Fluor Econamine
			DEA	DEA
		S,NS	Hindered amines	Flexorb
			DIPA or MDEA	ADIP
			Potassium methyl alpha aminopropionate	Alkazid
PHYSICAL	AB	NS	MDEA	MDEA
			Propylene carbonate	Fluor Process
		S,NS	N-Methyl-2-Pyrrolidone	Purisol
			Refrigerated methanol	Rectisol
			Dimethyl ether of polyethylene glycol	Selexol
			n-oligoethylene glycol and methyl isopropyl ethers	Sepasolv MPE
PHYSICAL/CHEMICAL	AD	S,NS	Molecular sieves (zeolites)	Molecular sieves
	AB	S,NS	DIPA or MDEA + Sulfolane	Sulfinol
			alkanolamine +methanol	Amisol
			Tertiary amine +physical solvent	Selefining

Table 30 Desulphurization/decarbonization processes (S: Selective NS: Non-selective)

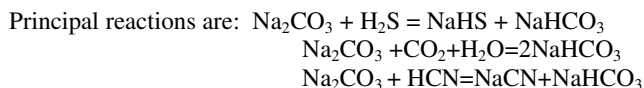
AB=Absorption
AD=Adsorption

❖ CHEMICAL ABSORPTION

VACUUM CARBONATE

This process uses a solution of sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3) to absorb the H_2S from the gas stream at a pressure ranging from 1 to 20 bar. The absorbent is regenerated by vacuum distillation (0.14-0.17 bar), which reduces the steam consumption, therefore H_2S is recovered in a concentrated usable form

H_2S removal efficiency reaches the 98% when a two stages process is used. The 93% of HCN and 5-7% of CO_2 is removed together with the H_2S [59].



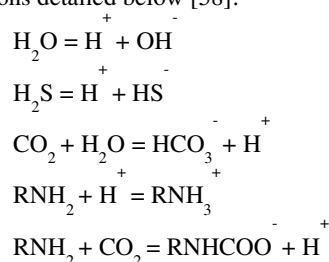
If some oxygen contacts the solution, consequent side reactions occur to form NaSCN and $\text{Na}_2\text{S}_2\text{O}_3$ [58]

It has to be considered that even trace amount of solvent in the gas may be harmful for the gas turbine, which makes this process less suitable for gas fuel cleaning.

AMINES

Removal occurs via reversible chemical reactions.

There are organic and inorganic solvents. Typical organic solvents are alkanolamines that remove H_2S and CO_2 via adsorption and the chemical reactions detailed below [58]:

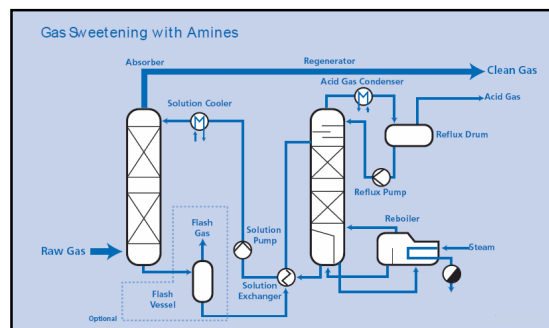


They are mainly used with streams where acid gas partial pressure or concentration is low. Operating temperature varies from -23°C to 77°C . Operating conditions will determine the selection of the most convenient amine.

Sour gas is conducted to a reactor where the amine absorbs the acid gas. Purified gas flows from the up part of the reactor while the acid rich amine is heated by hot regenerated lean amine in the heat exchanger. Amine regeneration occurs in the wet stripper where low pressure steam (3-3.8 bar and $135\text{-}142^\circ\text{C}$) is injected and acid gases are released. Steam on the acid gas stream is condensed and returned to the column. Hot regenerated lean amine is cooled and circulated to the absorption tower, completing the cycle.

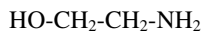
Figure 44 Gas sweetening with amines Source: Lurgi

During the amine regeneration, temperature has to be controlled in order to avoid corrosion problems. The temperature at the bottom of the stripper is usually 110°C to 116°C



This technology is indicated for low pressure sulphur removal. Main amines used in this process are MEA, DGA, DEA and MDEA

MONOETHANOLAMINE (MEA)

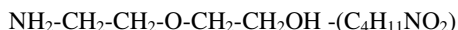


Used in low pressure treating applications and in operations requiring stringent outlet gas specifications. For use, it is 10% to 30% diluted in water. Acid gas loading is usually limited to 0.3-0.4 moles of acid gas per mole of amine for carbon steel equipment.

It is in general not preferred for gas cleaning because of its high heat of reaction and lower acid gas carrying capacity. In addition MEA reacts irreversibly with COS and CS₂

The Sulfinol process uses a MEA solution working at around 30°C and at a pressure varying from 0-70 bar. It removes in more than 98% the H₂S content of the gas but COS or HCN produce the degradation of the solvent[58][59].

DIGLYCOLAMINE (DGA)



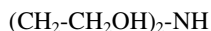
This technology is preferred when there is a need of COS removal in addition to H₂S and CO₂ from the gas stream. Solvent is diluted in water in a proportion of 40%-60% mass. Acid gas loading can be one per one mole. It has preference for CO₂ rather than for H₂S

It usually operates without any upper limit on pressure and at a temperature ranging from 32 to 105 °C for the absorption and around 120 -140°C and between 0.3 and 1 bar at the regeneration tower.

DGA has a high heat of reaction and very high gas carrying capacity as well as good potential for COS absorption. It is not corrosive to carbon steel.

The main process using this solvent is called Fluor Econamine [58].

DIETHANOLAMINE (DEA)



Typically used under high pressure conditions and diluted in a 25%-35% mass percent range. Acid gas loading for carbon steel equipment is 0.3-0.4 moles of acid gas per mole of amine. As it is a secondary amine it has less affinity for CO₂ and H₂S. In general, DEA is less corrosive than MEA, however, there are corrosion problems associated to its use because DEA reacts with CO₂ to form corrosive products.

Low heats of reactions and high acid gas carrying capacity results in a lower energy requirements. However it doesn't present high selectivity for H₂S removal from streams with CO₂ [58][59].

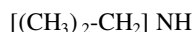
METHYL DIETHANOL AMINE (MDEA)



Has higher efficiency for H₂S than for CO₂ removal. Used solved in water at 30-50% mass. Due to reduced corrosion problems, acid gas loadings can reach the 0.7-0.8 mole acid gas /mole amine. As it is a tertiary amine it has less affinity for CO₂ and H₂S than DEA. It has a lower vapour pressure, lower heats of reaction and higher resistance to degradation.

This solvent is used in the Sulfinol-M process (mixed with Sulfolane). This amine is used as ADIP process absorbent when high selectivity is required. CO₂ absorption can be reduced to 10-30%. It can be used as well in pressure swing plants for bulk acid gas removal.
[58][59]

DIISOPROPYLAMINE (DIPA)



This solvent is used in the ADIP and in the Sulfinol-D process (in the last one, solvent is mixed with Sulfolane). It presents a high selectivity for H₂S absorption in streams with CO₂ whose capture is in the range 20-60%.

Operating conditions are 20-40 bar and a temperature varying from 20 to 60°C. The solvent is used in water solution[58].

Main advantages of this process are the high efficiency on H₂S removal, the low steam consumption (0.4-2.8 ton/ton acid gas removed), and the resistance of the solvent against degradation. Besides, the non-corrosive nature of the solvent allows the use of carbon steel equipment[58][59].

We can summarize most relevant amines properties for H₂S and CO₂ capture in the next table[65]:

AMINE	MEA	DEA	DGA	MDEA	DIPA
Boiling point (°C)	170.5	269	221	247	84
Freezing point (°C)	10.5	28	-12	-21	-61
Concentration in the solution (% mass)	12-20	25-35	40-60	30-50	30-50
Acid gas loading mole/mole amine	0.3-0.4	0.3-0.7	0.3-0.4	0.7-0.8	0.45
ΔH for H₂S (kJ/kg)	1281	1189	1570	1214	
ΔH for CO₂ (kJ/kg)	1922	1520	1729	1398	
Ability to preferentially absorb H₂S	No (0.89*)	Under some conditions (2.27*)	No (<1)	Under most conditions (3.85*)	Under most conditions

*REPSOL YPF :

$$\text{Selectivity} = \frac{[(\% \text{mol H}_2\text{S})_{\text{feed}} - (\% \text{mol H}_2\text{S})_{\text{treated}}] / (\% \text{mol H}_2\text{S})_{\text{feed}}}{[(\% \text{mol CO}_2)_{\text{feed}} - (\% \text{mol CO}_2)_{\text{treated}}] / (\% \text{mol CO}_2)_{\text{feed}}}$$

Amines can get contaminated by heat stable salts (strong acid anions forming a salt with the amine molecule), by degradation (breakdown of the base amine molecule), by chemicals (as corrosion inhibitors or anti-foam chemicals from upstream pipeline), by hydrocarbons from the gas stream and by particulates (iron sulphides, metals from corrosion, charcoal from amine filters and catalyst fines from upstream units) [66].

Main problems that amine based desulphurization unit can present are:

- Corrosion
- Amine degradation
- Foaming

Corrosion is caused by de acid gases in solution with the amine and water in combination with high temperatures. To avoid it, the use of special materials, corrosion inhibitors and lower operational temperatures have to be considered.

Main agents of the amine degradation are the oxygen (causing oxidation), sulphur compounds (COS or sulphur oxides), contaminants in the make up water (as chloride, magnesium, sulphate, bicarbonate ions, sodium or potassium) and derived contaminants deriving from the reaction of the CO₂ with the amine.

Foaming origin can be on a suspension of solids (products of the corrosion), liquid hydrocarbons or any other strange material (oil, inhibitors, impurities in the make up water or charcoal).

Instead of organic amines, inorganic solvents as potassium carbonate, sodium carbonate and aqueous ammonia can be used for the gas sweetening, being the potassium carbonate the most popular

FLEXORB SE

Some sterically hindered amines (amines with a bulky alkyl group attached to the amino group) have been developed as a replacement of MDEA. They present high H₂S selectivity, lower circulation rate and lower regeneration temperature (110°C). Besides, they don't cause carbon steel corrosion [67].

Selectivity depends on the hindered amine used. Moderately hindered amine removes all the CO₂, H₂S and organic sulphur impurities. However, severely hindered amines give high H₂S absorption capacity in the presence of CO₂.

H₂S concentration in the clean gas can be as low as 10 ppm. Operating conditions are similar to the MDEA process [68].

HOT POTASSIUM CARBONATE



In a solution of water in a proportion of a 20-40% mass, it is typically used for the CO_2 removal from a gas stream. It is activated by the presence of an amine (DEA). It is not suitable for streams with low CO_2 content because it would be more difficult to regenerate if the CO_2 is not present.

Operational temperatures vary from 70-126°C, close to the atmospheric boiling point of the solvent, which diminish the required input of heat for the solvent regeneration. Pressure of the process is around 22-70 bar but it can reach 137 bar.

Carbonyl sulphide is hydrolyzed to hydrogen and carbon dioxide. Ammonia is absorbed by potassium carbonate solutions.

Since H_2S is more soluble than CO_2 , H_2S is absorbed and stripped faster which allows a partially selective H_2S removal reaching the 90-95% of H_2S capture while CO_2 removal is restricted from a 10% to a 40%. However, for a non-selective process, efficiencies over 99% can be reached.

The main advantages are the low cost of the chemical, simplicity of the system and the low steam rate required for the stripping process.

Main disadvantage is the lower levels of H_2S removal comparing with other processes besides the foaming, and the corrosion and erosion caused by the released potassium present in the product gas.

The processes using this solvent are Benfield, Catacarb, Flexorb HP and Giammarco-Vetrocoke [59]

Catacarb uses a catalyst and a corrosion inhibitor as additives. The purity of the product is higher than in the uncatalyzed process (Benfield) while the steam consumption is lower. For Catacarb and Benfield processes, the minimal partial pressure required for CO_2 is 2.1 to 3.4 bar but Benfield ensures optimal operation for a CO_2 partial pressure of 7 bar [69].

Hindered amines are used in the Flexorb HP process to promote the CO_2 absorption.

Giammarco-Vetrocoke process is characterized by the utilization of an organic activator (glycine) that catalyzes CO_2 absorption.

ALKAZID

Alkazid process uses a solution of a salt of a strong inorganic base and a weak organic non volatile acid to absorb H_2S and CO_2 . Three types of solutions are used:

Alkazid M: to absorb H_2S or/and CO_2 depending on if they are alone or together in the gas.

Alkazid dik: To selectively remove H_2S when CO_2 is present.

Alkazid S: For gases containing other impurities (HCN, ammonia, carbon disulfide, mercaptans...)[68]

The acid gas load varies from 10-15 vol/vol of caustic for best removal of H_2S . H_2S final concentration can be around 0.07-0.1%

Optimum absorption temperature is about 5°C but it can be increased up to 30 °C. Stripping temperature is around 105 °C. Absorption and stripping occur at atmospheric pressure.

Problems of steel and aluminium corrosion can appear, as well as foaming. Besides, any oxygen entering into the system forms thiosulfates in the solution destroying its effectiveness.

❖ *PHYSICAL ABSORPTION*

Physical absorption is based on the high solubility of acid gases in the organic solvent. In general solubility increases as the temperature decreases and the pressure increases. Physical absorption methods are used at low temperatures and at pressures greater than 3.5 bar, in streams with low hydrocarbon content. These solvents remove COS from the stream as well as CO_2 when its partial pressure is high enough. Most of the physical sorbents present high H_2S selectivity.

The sorbents are regenerated by [65]:

- Multi-stage flushing to low pressure
- Regeneration at low temperature with an inert stripping gas
- Heating and stripping of solution with steam/solvent vapour.

Main physical absorption processes are Selexol, Purisol, Rectisol, Sepsolv MPE, Estasolv and Flour process.

FLUOR PROCESS



It uses a propylene carbonate as sorbent. Regeneration is carried out by flashing the rich solution through several stages.

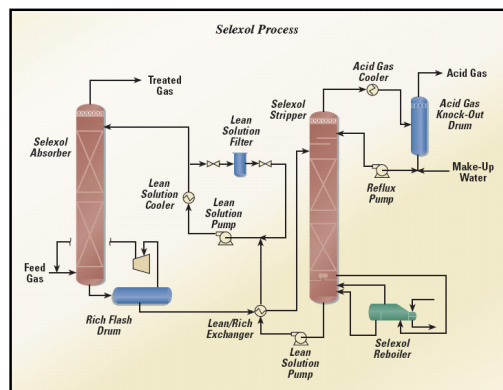
The acid gas load of the physical solvent depends on the partial pressure of the acid gases in the feed stream. The absorption process is favoured by high pressures (58-70 bar) Final concentration of H_2S can reach the 4 ppmv and the CO_2 less than 0.3%mol [65]

SELEXOL

Uses Union Carbide's Selexol solvent made of a dimethyl ether of polyethylene glycol. It is inert and it does not undergo degradation. Solvent is regenerated either thermally, by flashing to lower pressures or by stripping gas. Operational conditions are 20-138 bar and a temperature below 175°C (typically between -5°C and 30°C). Besides CO_2 and H_2S , it removes as well HCN, COS and heavy hydrocarbons. Acid gas concentration in the flow ranges from 5 to 65%vol.

Figure 45 Selexol process Source: UOP LLC

Selexol is applied for selective removal of H_2S and COS plus optional plus bulk removal of CO_2 . However, the relative solubility of H_2S in the solvent is four times that of the COS, so most of the COS will be removed with the CO_2 stream if it is not previously hydrolyzed.



One of the inconveniences of this process is the high electricity consumption to keep high pressure conditions. On the other hand, regeneration is easier in the stripper column with low steam consumption[59].

The Sepsolv process, that uses n-oligoethylene glycol and methyl isopropyl ethers as a solvent, has similar characteristics than Selexol and one solvent can be replaced by the other without equipment modifications[59].

PURISOL

N-Methyl-2-Pyrrolidone (NMP) is used as physical solvent. This process is used in a selective desulphurization of low temperature gases. Besides CO_2 and H_2S , it removes as well HCN and NH_3 . Sulphur compounds are first converted into H_2S which is selectively absorbed by the solvent.

Operating absorption pressure is around 70 bar and a temperature varying from 27°C to 40°C [59].

RECTISOL

A refrigerated methanol acts as a selective solvent to remove acid gases (CO_2 , H_2S and COS) and other substances as NH_3 , HCN and hydrocarbons.

Refrigeration is required to keep the temperature in the range of -38°C to -17°C in the absorbers and up to 65°C in the regenerator. Pressure oscillates between 22 bar and 170bar.

The process can be configured as a non-selective or selective process

In the selective process the feed gas is pre-cooled and purified in the column. A portion of the CO₂ loaded methanol is flashed in successive stages. While flash gases are re-compressed and recycled to the absorber, the regenerated methanol is driven to the top of the enrichment column. Same process follows the H₂S loaded methanol that, once purified, is fed into the middle of the H₂S enrichment column. To strip the CO₂ from the methanol, N₂ is used. The H₂S rich methanol is warmed up and fed into the regeneration column. Steam will complete the stripping of acid gases.

Final concentration of H₂S is typically 0.1 ppm and a few ppm of CO₂ are present as well in the clean gas.

❖ *PHYSICAL ADSORPTION*

MOLECULAR SIEVES

Crystalline sodium-calcium aluminosilicates (zeolites) can be used for selective removal of H₂S and other sulphur compounds.

In this process the gas flows through the fixed bed of molecular sieve at ambient temperatures and pressures ranging from 14 to 82 bar. H₂S, COS and other impurities are removed. When the bed becomes saturated, is regenerated at higher temperatures (290°C) with a slip stream of purified gas.

For high H₂S content streams, two bed absorbers are used. Final H₂S concentration can be as low as 4ppm. CO₂ can be removed with the H₂S but the concentration of carbon dioxide in the sour gas has to be very low. However, selective removal of H₂S in presence of CO₂ is possible[59].

❖ *COMBINED PHYSICAL/CHEMICAL PURIFICATION PROCESS*

These methods use a mixture of alkanol amines with methanol resulting in an improved physical absorption thanks to the methanol and a high chemical reactivity thanks to the amine.

General properties are a great H₂S and CO₂ removal level and low regeneration temperature. Besides, the solvent is not corrosive so carbon steel material can be used.

Most used amines are DIPAM (di-Isopropylamine) and DETA (di-Ethylamine).

SULFINOL

This process uses a mixture of Sulfolane, DIPA or MDEA and water, which allows the chemical and physical absorption. The acid gas loading and the required energy for regeneration is lower than in pure chemical absorption processes. Selective absorption of H₂S and COS in presence of CO₂ is possible.

Operational pressure in the absorber vary from slightly above atmospheric pressure to around 97 bar . High pressure favours physical absorption. [59]

AMISOL

It uses a mixture of methanol and MEA, DEA, diisopropylamine (DIPAM) or diethylamine. H₂S removal can be whether selective or non, being removed in the last case together with CO₂, and COS

Operational pressure in the absorber is around 14 bar at ambient temperature. For regeneration, the temperature might be kept under 100°C. Because of the high volatility of the solvent, both columns require water wash stages at the top, in order to absorb vaporized solvent which is recuperated via distillation.

H₂S can be removed to 0.1ppm and CO₂ to less than 5ppm [58].

SELEFINING

Uses a tertiary amine mixed with a physical solvent to promote selective H₂S removal. The amine reacts with the CO₂ in presence of water. Controlling the presence of water, the CO₂ removal can be controlled.

C.4.HOT GAS CLEANUP

4.1. Particulate removal

With this technology, particulates are removed as a dry solid and cooling of the gas is not required. Temperature can be above 500°C and typical pressures are 15-25 bar.

There are different options for the particulate removal: methods based on barriers or on external forces

METHODS BASED ON BARRIERS

HIGH TEMPERATURE FABRIC FILTERS

This system can remove fly ash particulate is accomplished by high-temperature fiber bag filters made of metal (as stainless steel) or ceramic fibres.

Besides the high operating temperature they present other advantages as a high resistance against abrasion and corrosion.

Particulate removal efficiency >99- >99.9999%
Particle size range 0.01- >100 µm

FIBRE	Generic name	Metal	Ceramic
	Trade name	Bekinox	Nextel 312
Recommended continuous operation temperature (°C) dry heat		450	1150
Water vapour saturated condition (moist heat) (°C)		400	1150
Maximum(short time)operation temperature (dry heat) (°C)		510	1427
Relative moisture regain in % (in 20°C and 65% relative moisture)		7.9	2.7
Resistance to alkalis		Very good	Good
Resistance to mineral acids		Very good	Very good
Resistance to organic acids		Very good	Very good
Resistance to oxidising agents		Very good	Excellent
Resistance to organic solvents		Very good	Excellent

Table 31 High temperature fabric filters [70]

CERAMIC FILTERS

Ceramic materials based in alumina, quartz or aluminum silicates allow high temperature filtration and good resistance against acids and oxidising agents.

Three types of ceramic filters can be distinguished [54]:

1. *Candle filters*: it is formed by group of 800-1500 ceramic cylindrical tubes that remove the particles from the pressurized gas at temperatures up to 900°C. However, creep problems can appear if work temperature surpass 700 °C Ceramic candle filters are commercially available for moderate temperature and pressure applications. The pressure drop of the gas vary from 0.04bar to 0.07bar
2. *Ceramic tube filters*: It has been used up to 900°C.
3. *Cross/parallel flow filters*: composed by a compact structure of thin ceramic plates. More efficient than candle filters.

Main degradation causes and mechanisms of these filters are mechanical, thermal and chemical shock, which causes most of the short-term failures. In a long term period, thermal exposure, temperature transients, bulk gas reactions, contaminants and flash ash interactions causes most of the failure problems.

HIGH TEMPERATURE METALLIC FILTERS

Operating temperature can be up to 450 °C under oxidant conditions or 600 °C if the atmosphere is reductive.

Metallic filters can suffer corrosion due to the Chromium and Nickel contained in the gas (Ni_3S_2 and H_2S). To avoid corrosion is advisable to work under 400 °C and concentrations of H_2S under 300ppm [54]

Removal efficiency : 95%

HIGH TEMPERATURE GRANULAR BED FILTERS

There are three options for pressurized and high temperature particulate removal with this technology: fluidized, packed or moving bed filters

In packed bed hot gases pass through a mass of filtering granules. These filters require frequent cleaning and regeneration of the filtering media as the filters quickly become plugged.

In moving bed filters, the bed is pneumatically moved which allows better interception of small particulate matter and filtering granule regeneration without interrupting the filtering operation. The granules of the bed leaving the reactor can be recycled back pneumatically after cleaning[71].

In fluidized bed, fluidization is kept by the hot gas flux. Operating temperature is around 900°C and particulate removal efficiency is 99%.

Removal efficiency: 99->99.99%

Particle size range >1 mm

METHODS BASED ON EXTERNAL FORCES

HIGH TEMPERATURE CYCLONES

With the temperature, the density of the gas decreases, as well as its dynamic viscosity. This increases the minimum diameter of captured particles. However, a set of several cyclones attain acceptable cleaning levels. This is the most used method in IGCC plants. Cyclones allow the recycling of the captured particles to the gasifier.

Operating conditions are 650-950 °C of temperature and a pressure up to 100 bar. The pressure drop ranges from 1 to 5 bars. The size of the captured particles is larger than 5 μm [54].

Removal efficiency: 75-99%

Particle size range: 5.0-100 μm

HOT SIDE ELECTROSTATIC PRECIPITATOR

The mechanism used to remove the particles is analogue to that of the "cold" EPS. They can be either plate or tubular.

Operating temperature range is usually 300-450°C but they can handle temperatures up to 700°C. The pressure varies from 5 to 15 bars.

Removal efficiency: 99->99.99%

Particle size range: 0.01- >100 μm

4.2. Chlorine compounds removal

The removal of chlorine compounds from the gas is important in order to avoid poisoning of a catalyst used further, downstream corrosion or hazardous emissions. Calcium or sodium based solvents have been identified as appropriate for HCl removal from hot gasification gases.

The efficiency of calcium based solvents as limestone (CaCO_3) or lime (CaO) is limited by the CO_2/HCl ratio in the gas. Therefore, the removal efficiency is lower when the gasification agent is air rather than oxygen. These solvents can give a satisfactory result at atmospheric pressure, however, the formation of CaS can displace the formation of CaCl_2 and the temperatures might be kept under 450°C[33][34].

Sodium based sorbents as sodium carbonate (Na_2CO_3) or sodium bicarbonate (referred as nahcolite)(NaHCO_3) show a high purification degree. In particular, sodium carbonate present an effective capacity of over 80% at temperatures ranging from 800-900°C [72].

Na_2CO_3 has been reported to have capacities over 80% at optimum operating temperatures between 400°C and 500°C. Furthermore, not significant influence of the pressure level (1-20bar) has been detected [72].

Other identified sorbents for HCl removal that are still in experimental stage are shortite ($\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$) and trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) that react with HCl at 523°C, being shortite more reactive than trona.

Experimental studies show that an eutectic melt of Li_2CO_3 and Na_2CO_3 reduces the HCl presence to 1ppm at 500°C. Alkalized alumina, operating at 625°C has been reported to have efficiency characteristics.

H_2S is removed together with the HCl when solid lithium, potassium or calcium carbonates, supported on lithium aluminate are used. HCl can be reduced to a concentration lower than 10ppm at 800°C and 15at [73].

4.3. Hot Gas Desulphurization (HGD)

A hot gas desulphurization process avoids the losses of heat associated to more traditional warm or cold gas desulphurization methods, thus such a process improves the thermal efficiency of an IGCC power plant, where normally the gas has to be re-heated before entering into the gas turbine. However, some difficulties complicate the commercialization of these systems. Sorbents are susceptible of particle break-up due to chemical changes and mechanical attrition. Besides, some components as zinc can vaporize. Finally, metals sulphates can be formed in side reactions[58]. Another disadvantage of these processes is that the final product is not H_2S but SO_2 which present more disposal problems.

Sorbent materials have to present the following characteristics (Westmoreland and Harrison,1976; Zeng 1999):

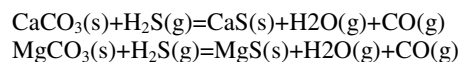
- Thermodynamically favourable for H_2S removal to desired levels in the specified operating conditions and for a certain gas composition
- Good theoretical capacity determined by stoichiometrics and kinetics.
- Stability at high temperatures and in a reducer ambient
- Regenerability
- Stability throughout sulfidization-regeneration cycles
- Reasonable cost

Sorbents can be classified in two groups[58]:

- ✓ Alkaline earth metal compounds: CaO ; limestone; dolomite;
- ✓ Transition metal compounds: FeO ; ZnO ; Zinc ferrite;

CALCIUM AND MAGNESIUM OXIDES

Calcium oxides are usually used together with magnesium oxides for *in-situ* sulphur removal. They fed into the gasifier as a carbonate (dolomite or limestone) where the following reactions occur:



Calcium carbonate sulfidization start at 600°C and at 880°C it reaches its maximum conversion level.

Because of thermodynamic limits, minimum reachable concentration of H_2S is about 100-500ppm. Besides MgS is non stable under gasifier conditions.

Regeneration of CaS and MgS requires high temperatures and the rate of regeneration is moderate[74].

Other oxide with similar characteristics of calcium carbonate is BaCO_3 . BaCO_3 sulfidization begins at 800°C and at 900 °C has capacity of removal of 95%. Besides the higher operating temperature, BaCO_3 is cheaper than calcium carbonates.

IRON OXIDES

Iron oxides present high sulphur removal capacity, low cost and good regeneration properties. It can be used up to 700°C when Fe₃O₄ is more stable.

Main inconveniences of this sorbent is the oxidation of FeO to FeO₂ at the beginning of the absorption and the formation of COS because of side reactions where FeS or H₂S combines with CO₂.

Equilibrium levels of H₂S are quite high for iron oxides between 400°C and 600°C degrees [74].

ZINC OXIDES

Zinc-based sorbents can reduce COS and H₂S to about 10ppm in coal gasification syngas. However, the composition of the gas affects the performance of the process because of the side reactions that may occur. It can be used up to 700°C to avoid Zn vaporization.

Sulfidization reaction occur between 500 °C and 700°C.: $\text{ZnO} + \text{H}_2\text{S} = \text{ZnS} + \text{H}_2\text{O}$

Acid gas load is around 13-19 kg. sulphur/100kg sorbent [58]

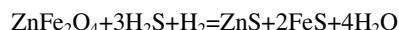
Sorbent is regenerated with air: $\text{ZnS} + 3/2\text{O}_2 = \text{ZnO} + \text{SO}_2$

Regeneration reaction is exothermic and high temperatures in the reactor can cause the formation of ZnSO₄ which, because of its bigger volume it will crumble the solid [74].

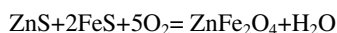
One of the processes based on this type of sorbent is the Z-Sorb which uses a promoted zinc oxide sorbent. An experimental study carried out at the gasification plant of Puertollano (Spain) shows how the high capacity of this type of sorbent (Z-Sorb III) to reduce the H₂S present in the coal gasification gas. Besides they point out that in order to avoid undesirable side reactions as Boudouard or methanation, space velocities of the gas must be kept over 3500h⁻¹ [75].

ZINC FERRITE

The zinc and iron contained in the ferrite sulfidize in a reaction where a mol of ferrite retains 3 mol of sulphur at temperatures under 650°C:



Ferrite is regenerated with the oxygen diluted with nitrogen in order to avoid the decomposition of the sorbent caused for temperatures in the reactor above 750°C:



However, if regeneration pressure is low and the presence of the SO₂ and O₂ in the gas is high, ferric and zinc sulphates can be formed. Ferric sulphate appears at temperatures under 480°C while zinc sulphates do it at temperatures under 600°C.

There are some inconveniences to use this sorbent to clean coal gasification gas. First of all the consumption of the hydrogen in the sulfidization reaction will decrease the energetic value of the product gas. Secondly, the presence of reducer gases as CO and H₂ with high CO/CO₂ ratios (mainly in gasifiers using pure oxygen) leads to a reduction of the zinc ferrite to iron oxide or iron, that react with CO to form iron carbide Fe₃C. Iron carbide formation reduces absorption capacity and breaks the solid because of the mechanic tensions caused by the difference of density [74].

ZINC TITANATE

This type of sorbent is still in laboratory study stage but it shows promising characteristics. Zinc titanates stabilises the ZnO against reduction to elemental Zn. ZnO supported by a TiO₂ matrix can be used up to 732°C. This configuration shows good mechanic properties and it tolerates the presence of HCl in the gas [74].

H₂S can be reduced to 20ppm in a fluidized bed reactor.

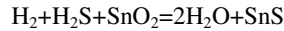
Main disadvantage of this system is the progressive loss of reactivity over multiple sulfidization/regeneration cycles above 650°C.

As for the ZnO sorbent, formation of ZnSO₄ during regeneration can crumble the solid.

TIN OXIDE

Sulphur is removed from the gas at a temperature ranging from 350°C to 500°C .

The reaction describing the process is:

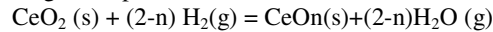


In order to avoid reduction of the tin oxide to elemental tin, the ratio of water to hydrogen about 1.5. For regeneration, superheated pressurized steam can be used.

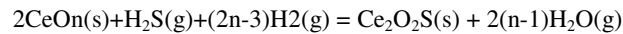
CERIUM OXIDE

The interest of using Cerium for desulphurization is justified by the fact that elemental sulphur is produced during regeneration.

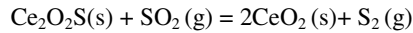
At high temperatures and in a reducing atmospheres the CeO₂ is reduced to CeOn(n<2) following the reaction:



Sulfidization occurs at around 800°C :



Regeneration is done with SO₂:



However, the limited capacity of desulphurization makes necessary a second desulphurization stage.

Other disadvantage is the consumption of Hydrogen during the reduction of CeO₂. On the other hand cerium oxides can work under high temperatures (over 700°C) in highly reducing gases, which is impossible for zinc oxides[76].

C.4. CO₂ CAPTURE

CO₂ is one of the main greenhouse gases and energy sector highly contributes to the emissions of this substance. The control of the CO₂ released to the atmosphere is a prior issue on most of the developed countries, principally on the signers of the Kyoto protocol. This is the reason of the increasing importance of technologies helping to remove CO₂ from the exhaust stream of fossil-fuel combustion. The different CO₂ capture methods can be classified in three groups:

Pre-combustion capture: The carbon monoxide of the fuel gas is shifted with steam to produce H₂ and CO₂. The carbon dioxide is then removed and the resulting fuel has a high Hydrogen content.

Post-combustion capture: The CO₂ is removed from the combustion flue gas before being discharged to the atmosphere.

Oxy-fuel combustion capture: If pure oxygen is used for combustion, the resulting exhaust gases are mainly CO₂ and water.

The principal methods for CO₂ capture are :

REMOVAL MECHANISM	PROCESS
CHEMICAL ABSORPTION	MEA
	DGA
	MDEA
	ADIP (DIPA+MDEA)
	Hindered amines
	Aqueous ammonia
	Alkali Metals
	Hot Potassium Carbonate
	Amino Acid Salts
	Lithium Zirconate
PHYSICAL ABSORPTION	Fluor process
	Purisol
	Rectisol
	Selexol
	Sepasolv MPE
CRIOGENIC	LT distillation
PHYSICAL/CHEMICAL ABSORPTION	Sulfinol
	Amisol
PHYSICAL ADSORPTION	PSA
	TSA
	ESA
	VSA
MEMBRANES	Polymeric
	Inorganic
OXY-COMBUSTION	
INNOVATIVE PROCESSES	Hydrate formation CO ₂ recycle combustion
	Chemical Looping combustion
	Ionic liquids

Table 32 Decarbonization processes

AB=Absorption
AD=Adsorption

(Methods in coloured cells have been already explained in section 3.2 as desulphurization/decarbonisation methods)

❖ CHEMICAL ABSORPTION

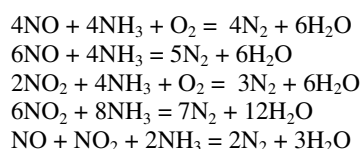
AMINES

Amines characteristics for CO₂ pre-combustion removal have already been explained in the section 3.2 where the methods for gas desulphurization and decarbonisation are treated. However, given the non-selectivity nature of most of the amines, they are commonly used only for post-combustion decarbonisation.

The principal inconvenience for post-combustion decarbonisation with amines is the low pressure of the flue gas which decreases the absorption rate. Primary and sterically hindered amines can absorb CO₂ at low pressure because of the high reaction energy but this result in high energy requirement to regenerate the solvent.

Another inconvenience is the oxygen present in the gas that can degrade the solvent and cause corrosion problems. The use of inhibitors of degradation and corrosion is required [77]

Sulfur or Nitrogen oxides can react with the amine to form salts. Therefore the content of sulphur oxides should be below 10ppm while NO₂ has not to surpass the 20mg/Nm³. In order to reduce the content of NO_x in the flue gas, they can be catalytically reduced with ammonia. Selective catalytic reactions (SCR) with ammonia are:



This process reduces around 90-95% the NO_x concentration. Catalyst operating temperature ranges from 150 to 600°C but the temperature must be kept under 400°C to minimize the formation of N₂O in side reactions.

Precious metal, base metal or zeolite catalyst can be used depending on the operating temperatures

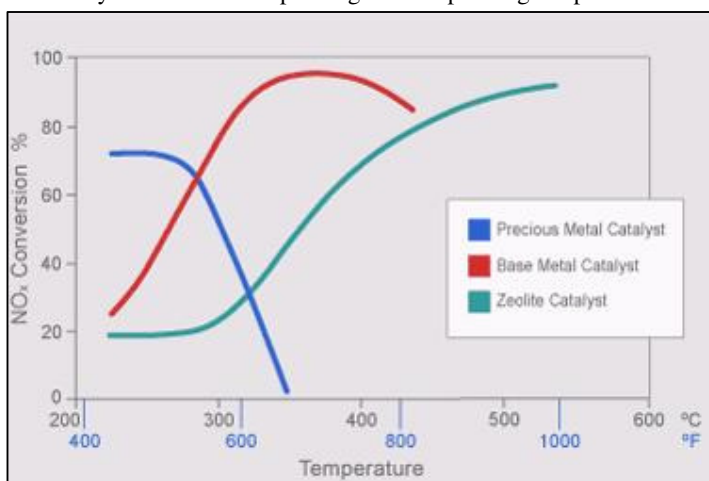


Figure 46 Catalyst for SCR at different temperatures [78]

AQUEOUS AMMONIA

Aqueous ammonia can absorb CO₂, SO₂ and NO_x. It is cheaper and it requires less regeneration heat than MEA. Steam consumption could be reduced by 49-64% from an MEA system [79][80]. In addition, aqueous ammonia sorption capacity is higher than MEA. Main products of this process are ammonium bicarbonate and the degradation forms of NH₃: ammonium nitrate and ammonium sulfate. Aqueous ammonia does not cause corrosion problem and there is no absorbent degradation.

The main inconvenience of this solvent is the high volatility of the ammonia that tends to leave the reactor with the exhaust gas. This problem can be solved by cooling the exit gas or washing with water or acid was, but this would increase the cost of the process. Besides, adsorption with aqueous ammonia is slower than with MEA [81].

ALKALI METALS BASED SORBENTS

Alkali metals hydroxides or carbonates (as NaHCO_3 , Na_2CO_3 or K_2CO_3) present interesting capacities for CO_2 absorption. They are resistant to degradation and they require less heat of regeneration than MEA [82]

POTASSIUM CARBONATE SOLUTION

Most of the potassium carbonate processes used for CO_2 removal have been already explained in the section 3.2. However innovative processes as potassium carbonate promoted by piperazine have been proposed for post-combustion CO_2 removal. This combination results in a fast removal process :1 to 5 times faster than MEA. Main advantages are the low regeneration heat required in comparison with MEA and the low volatility of the solvent. However, piperazine is more expensive than MEA [83]

AMINOACIDS SALTS

Certain potassium salts as potassium glycinate, potassium taurate and potassium sarcosine [84][81] have been identified as good absorbers of CO_2 , presenting higher absorption capacity than MEA and better resistance to degradation.

Amino acids have the same functional groups as alkanolamines, and can be expected to behave similar towards carbon dioxide, but do not deteriorate in the presence of oxygen. Besides, the salt function ensures the non volatility of the substance at the stripper [85]

LITHIUM ZIRCONATE

Lithium zirconate (Li_2ZrO_3) reacts with CO_2 at temperatures between 500°C and 700°C which makes it suitable for CO_2 pre-combustion capture systems. It has a large capacity for CO_2 absorption and its performance gets improved with potassium carbonate and Li_2CO_3 addition.

❖ *PHYSICAL ADSORPTION*

Physical adsorption methods are based on the capacity of certain sorbents (as zeolites, alumina or activated carbon) to attract the CO_2 to the sorbent surface under determinate conditions. Regeneration is carried out by variation of the pressure (PSA and VSA) or of the temperature (TSA). More innovative processes as ESA uses electric current for regeneration.

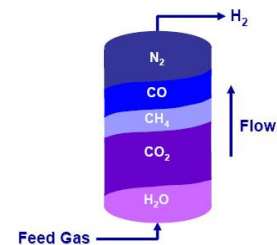
The low capacity and CO_2 selectivity of the available adsorbents doesn't allow the application of this technology to large scale flue gas decarbonisation. However, adsorption may be successful when combined with another capture technology [86]

PRESSURE SWING ADSORPTION (PSA)

This process is widely used for Hydrogen purification. It consists in a number of connected vessels containing the adsorbent material (usually zeolite for Hydrogen purification). Under pressure, the bed adsorbs the contaminant gases that are later released when the pressure diminish. Gases as H_2 , He, O_2 , N_2 and Ar are not or lightly absorbed. CO , CO_2 and CH_4 are partially adsorbed while moisture is heavily adsorbed [58]. PSA is used to pre-combustion removal of CO_2 from gases that have undergone shift reaction, thus most of the CO has been transformed into H_2 and CO_2 . The product gas will be pure Hydrogen (up to 99.999%).

In general, PSA operation can be summarized in five steps(UOP,1991):

1. **Adsorption:** a constant flow of pressurized gas is fed into the vessel where the adsorber retains the contaminants. Separation can be based on equilibrium, or kinetic selectivity.
 - a. **Equilibrium selectivity:** the more strongly adsorbed component of the gas stream are retained while less strongly adsorbed species leaves the vessel. This is mainly used for gas purification.



Relative Strength of Adsorption of Typical Impurities

Non-Adsorbed	Light	Intermediate	Heavy
H ₂	O ₂	CO	C ₃ H ₆
He	N ₂	CH ₄	C ₄ H ₁₀
	Ar	C ₂ H ₆	C ₅ +
		CO ₂	H ₂ S
		C ₃ H ₈	NH ₃
		C ₂ H ₄	BTX
			H ₂ O

Table 33 Relative Strength of Adsorption of Typical Impurities [58]

- b. **Kinetic selectivity:** The faster diffusing species are retained by the adsorbent while the product stream contains the components with slower diffusion. The obtained gas is less pure than in the equilibrium selectivity case, therefore this type is used mainly for bulk separations
2. **Co-current depressurization:** feed is stopped and pressure is reduced by removing the gas which flows in the same direction as the feed flow (from the bottom to the top). Part of the recovered gas is used for purging and partial pressurization of another unit.
3. **Counter-current depressurization:** Pressure is further reduced by recovering the gas that flows now from the top to the bottom). Lower pressure favours sorbent regeneration. Part of the adsorbed gases is recovered as tail gas.
4. **Purge:** In order to complete the regeneration of the sorbent a counter-current stream of product gas flows through the vessel cleaning the sorbent.
5. **Repressurization:** Purified gas is fed from the top of the vessel to rise the pressure to the feed gas pressure level.

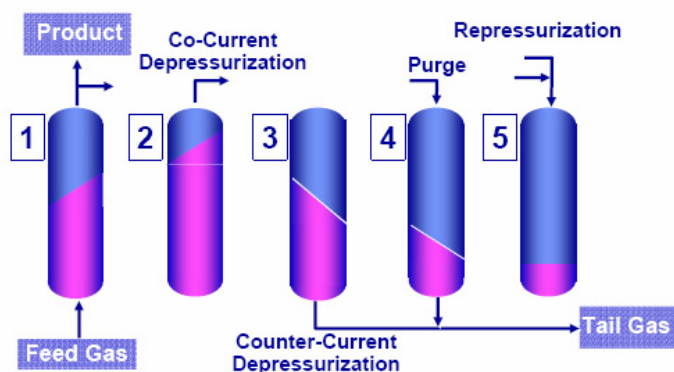


Figure 47 PSA

Operation [87]

A minimum pressure ratio of 4:1 between adsorption and desorption is required. Desirable feed pressure is 14-28 bar. The pressure drop from feed to product is relatively small around 0.5 bar [58]

A particular case of the PSA is the Vacuum Swing Adsorption (VSA) where adsorption pressure is lower than for the PSA process and desorption occurs under vacuum conditions to allow the total regeneration of the adsorbent.

TEMPERATURE SWING ADSORPTION (TSA)

TSA is an adsorption process where adsorption and regeneration are regulated by the temperature that has to be increased for the regeneration of the sorbent. The general process is very similar to PSA.

There are two options for heating the bed: feeding purge gas into the vessel, purging using superheated steam. If gas is used for purge, part of the contaminants are removed from the sorbent however if steam is used other method to remove the contaminants has to be foreseen, given that adsorbed gases are not soluble in steam. On the other hand the calorific capacity of the gas is lower than the one of the steam and in consequence more quantity of gas has to be used. Another option is the indirect heating of the bed by avoiding the contact between the primary heat transfer fluid and the adsorbent using an internal heat exchanger.

The main advantage of TSA is that desorption of hardly adsorbed species is easier than with the PSA method. However, the time required for heating and cooling the adsorber makes this process slower than PSA. In addition, the bigger size of the vessels necessary for TSA increases the total cost of the installation. However, the operating cost is lower than with PSA given that not mechanical energy is required and the heat can be recovered from other parts of the process.

ELECTRICAL SWING ADSORPTION (ESA)

This technology is not commercial yet but the bench scale essays show promising results. The main characteristic of ESA is the use of a low voltage electric current for sorbent regeneration which results in a faster process that in addition presents the advantage of the atmospheric operating pressure and a minimal variation of the temperature of the system.

Activated carbon fibers are used as a sorbent. It presents higher adsorption capacity than granular activated carbon because of the greater volume of its micropores. The high conductivity of this material favours the rapid and efficient desorption of the adsorbed gases [88]

❖ *CRYOGENIC DISTILLATION*

This process consists on the liquefaction of CO₂ to separate it from the gas stream. The condensation temperature of each component depends on its partial pressure in the sense that if partial pressure decreases, then the condensation temperature decreases as well.

In a first stage, H₂O has to be removed in order to avoid ice formation. Besides, in post-combustion processes, gases as SO_x, NO_x and steam have to be removed before cooling in order to avoid their condensation and further contamination of the CO₂ stream.

Three different loops with tree different refrigerants (R32, Ethylene and Methane) compose the cooling system [89].

The main disadvantage of this technology is the amount of energy consumed. However, as an advantage it has to be mentioned that produced liquid CO₂ is ready for pipeline transport.

❖ *MEMBRANES*

A membrane is a thin barrier which allows selective passage of different species through it. Most of the membranes operate separating H₂ rather than CO₂ from the gas stream. These membranes are used on pre-combustion capture given that a shifted and desulphurized gas is made up mainly by hydrogen and carbon dioxide. For post combustion capture, membranes separating CO₂ from the gas (mostly nitrogen) are used. Membranes for oxygen separation have as well an important role for carbone capture if oxy-combustion is used. This type of membranes is treated later in the section "Oxygen separation".

If compared with traditional technologies, membranes present certain advantages for bulk CO₂ removal, for instance the size is more reduced given that the membrane area required depends more on the percentage of gas removed than on the feed flow. Other remarkable advantages are the lower installation and operational costs, operational simplicity, reliability and efficiency[90]

Membranes can be classified in polymeric and inorganic:

Polymeric membranes: They are the only commercially available option for CO₂ separation from flue gases. They are based on cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates or polyetherimide [90]. Because of the thermal, mechanical and chemical instability of polymeric membranes under high pressure and temperature conditions, they are not an alternative for CO₂ capture in large-scale power production.

Relative Membrane Permeabilities

Relative Permeability	High	Medium	Low
Components	H ₂	C ₁	C ₂ +
	H ₂ O	O ₂	N ₂
	H ₂ S		
	CO ₂		

Table 34 Relative membrane permeabilities [91]

Inorganic membranes: Inorganic membranes are highly stable at high temperatures. They can be destined to the separation of hydrogen from CO₂/CO/CH₄/H₂O or to the separation of CO₂ from H₂/H₂O/CH₄/H₂O. The cost of inorganic membranes is higher than for polymeric but their expected life is longer, even in corrosive environments. In general inorganic membranes for H₂ or CO₂ separation can be classified as follows:

	Type	Compounds	Other classification	Gas separation
DENSE MEMBRANES	Metallic	Pd Alloys		H ₂
	Ceramic	Perovskites		H ₂
		Silica		H ₂
POROUS MEMBRANES	Metallic	Pd, Rh, Ir, Pt, Ni		H ₂
	Micro porous ceramic	Amorphous microporous silica, Alumina, zirconia, titania	Sol Gel	CO ₂ or H ₂
			CVD	
	Carbon	Carbon	MSCM	H ₂
			ASCM	
	Zeolite	Zeolite		CO ₂ or H ₂
	Glass			H ₂

Table 35 Inorganic membranes

– **Dense Pd-based membranes:** Their efficiency separating H₂ from gases mixture has been proved. They are 100% selective to H₂ and they resist temperatures from 300 to 600°C. The main disadvantages of this membrane is the low flow and the degradation of the membrane caused by sulphur compounds. are used. In addition, operation at lower temperatures can cause stress in the membrane because the hydrogen can become locked inside the palladium. Besides Pd, other metals such as tantalum, niobium and vanadium can be used as a base for dense membranes for H₂ separation. [92]

– **Dense Perovskite-based membranes:** This type of membranes is mainly used for O₂ separation but hydrogen can selectively permeate through it. Dense ceramic membranes present high stability under high temperature (up to 900°C) and high pressure conditions. However its chemical stability is compromised in presence of CO₂ or H₂S. They are 100% selective to hydrogen but the flux is rather low. They are relatively inexpensive compared to Pd membranes.

– **Porous metallic membranes:** Pd, Rh, Ir, Ru, Pt, Ni, Co, Fe, Cu and Ag are the metals used for the fabrication of porous membranes. High permeance levels can be reached, however, the selectivity has to be improved. Their main advantage is that they are not affected by the presence of steam in coal gas streams and that they can generally achieve higher H₂ fluxes than ceramic membranes at lower temperatures [93].

– **Amorphous microporous silica membranes:** Silica membranes have high, chemical and structural stability in oxidizing or reducing environments. They are employed usually for high temperature H₂ or CO₂ separation from N₂ or CH₄. However, the selectivity H₂/CO₂ is lower. Another inconvenient is the thermal instability of these membranes in water vapour containing atmospheres where pore volume and surface area can be reduced if the temperature rises over 500°C. Two types of silica membranes can be distinguished depending on how the membranes have been prepared: sol gel and CVD (chemical vapour deposition). CVD membranes show higher selectivity than sol gel, but their permeability is lower [94].

– **Carbon membranes:** Most important application of these membranes is the separation of N₂ from air but they are used as well for H₂ separation from gasification gas. These membranes can be classified as Carbon Molecular Sieve Membranes (CMSM) and Adsorption Selective Carbon Membranes (ASCM). CMSM micropores allow the separation of small molecules from the larger ones. For CMSM membranes, the hydrogen permeability is low but their high thermal stability makes these membranes suitable for CO₂ separation from flue gases from power plants. The ASCM type selectivity is based on the surface diffusion mechanism. They can operate at ambient temperature [92][94].

– **Zeolite membranes:** The separation with these membranes is based on molecules size and polarity among others. Molecules with higher molecular weight permeate better at low temperature while at high temperature lighter molecules show better permeability. This is the reason why H₂ permeates better at higher temperatures (about 500°C) while CO₂ does it at lower temperature. In general these membranes show high permeability and low selectivity [95].

– **Glass membranes:** They present a good thermal and chemical stability but they are highly fragile. The permeability of H₂ is high but the selectivity is very low [94].

The following table summarizes the main properties of relevant hydrogen selective membranes:

	DENSE POLYMER	MICRO POROUS CERAMIC	DENSE METALLIC	POROUS CARBON	DENSE CERAMIC
Temperature range(°C)	<100	200-600	300-600	500-900	600-900
H ₂ selectivity	low	5-139	>1000	4-20	>1000
H ₂ flux (10 ⁻³ mol/m ² s) at dP=1bar	low	60-300	60-300	10-200	6-80
Stability issues	Swelling, compaction, mechanical strength	Stability in H ₂ O	Phase transition	Brittle, oxidising	Stability in CO ₂
Poisoning issues	HCl,SOx		H ₂ S, HCl, CO	Strong adsorbing vapours, organics	H ₂ S

Table 36 Hydrogen selective membranes. Adapted from [96]

Recent development work has focused on the following technological options that are applicable to both CO₂/N₂ and CO₂/H₂ separations (IPCC 2005):

- Amine-containing membranes [97].
- Membranes containing potassium carbonate polymer gel membranes [98].
- Membranes containing potassium carbonate-glycerol [99].
- Dendrimer-containing membranes [100].
- Poly-electrolyte membranes [101].

The membrane separation system can present a single stage (one membrane) or a multistage flow scheme (several membranes) depending on recovering objectives and economic reasons. For CO₂ a single stage will remove less than the 50%. A multistage system afford higher recovery rates but increases the installation cost. In addition, recompression facilities between stages increases the ancillary power consumed by the plant. In a multistage schema, membranes can be connected in series or in parallel depending on the flow rates and purity requirement.

The series flow configuration is adequate for systems that provide high recoveries for a determinate feed rate. Contrarily, parallel flow configuration allows higher feed rates for the same recovery.

❖ OXY-COMBUSTION

Oxycombustion is one of the most promising and less developed technologies for CO₂ capture. It consist on burning the fuel with pure oxygen mixed if necessary with CO₂ in order to control the combustion temperature. The combustion products are CO₂, steam and the excess of oxygen.

Theoretically the capture ratio is 100% for combustion for pure hydrogen, however, usually the purity of the oxygen stream is around 95% and the rest are inert gases as N₂ and Ar. If those gases are separated from the CO₂ stream (i.e. via cryogenic purification) around a 25% of the vent stream will be carbon dioxide, which decreases the capture ratio to 95%. However, if no purification is applied, the compression of the inert gas remaining in the CO₂ stream will cause an important loose of efficiency. Another option is to purify the gas with a Selexol process after combustion, which increases the capture rate to 99.7% [102].

Main disadvantage of oxycombustion is the necessity of an Air Separation Unit (PSA, polymeric membranes or cryogenic distillation) which consumes an important part of the ancillary power. Other inconvenience is the early stage of development of the gas turbines for oxycombustion. Gas turbines are designed to work with air and the change to an oxygen-CO₂ mixture requires the adaptation of the design of the compressor, combustor and the turbine. For example the gas density is 50% higher than air and the heat ratio is lower which means that temperature variations are lower after compression or expansion. As a result, the optimal compressor ratio is rather higher than for air(30-35 compared to 15-18). Additional changes have to be done in the turbine materials system in order to adapt it to the higher combustion temperatures.

❖ INNOVATIVE PROCESSES

The increased importance of carbon capture technologies has lead to a growing number of research projects in this area. As a consequence new capture methods appear showing a promising future on the power generation sector.

➤ Bechtel National, Inc., with Los Alamos National Laboratory and SIMTECHE have developed a technique to remove CO₂ from a shifted syngas stream as a solid hydrate in a water slurry at near freezing temperatures. The gas stream is pressurized to around 70 bar and then is fed into a water saturated reactor at low temperature where ice crystals trap the CO₂. Water is then separated and recycled to the reactor while the produced pressurized CO₂ is ready for transport. (Deppe et al, 2003) The energy consumed by this technology is rather lower than the amine based systems consumption but it is still significant because of the cooling energy requirements. [103]

➤ In chemical looping combustion, to allow separated oxidation and reduction reactions, a metal oxide is used as an oxygen carrier, therefore, there is not contact between fuel and combustion air. The metal oxide is reduced at the reduction reactor where the fuel is oxidized. This reaction occurs in the fuel-reactor and is endothermic. After reduction, the oxygen carrier is fed into the oxidation reactor for exothermic re-oxidation. After leaving the air-reactor, the metal oxide is separated from the hot gases stream in a cyclone. [104]. The suitable temperature of air reactor should be between 1050–1150°C and the optimal temperature of the fuel reactor be between 900–950°C [105].

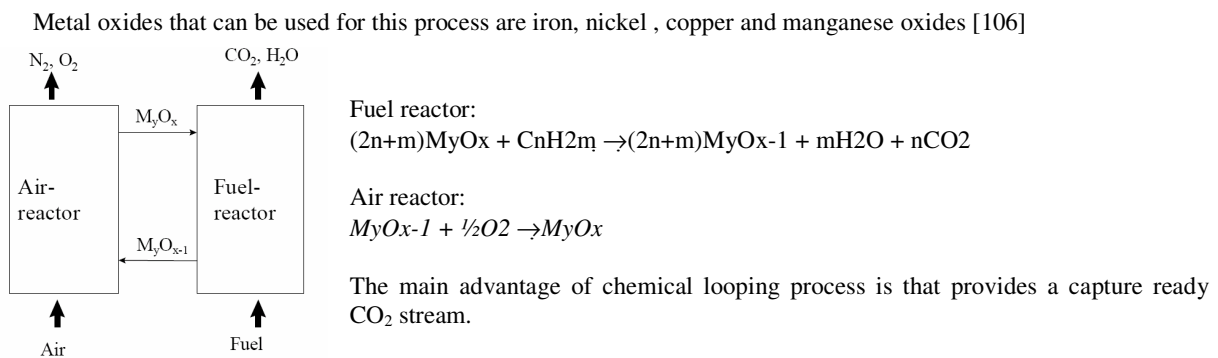


Figure 48 Chemical looping combustion

➤ Ionic liquids are a class of organic salts that are liquid at or near room temperature. Ionic liquids are also non-volatile and non-flammable. Physical and chemical properties of Ionic Liquids may be tailored to enhance the selectivity of a desired reaction.

Carbon dioxide has a much higher solubility in imidazolium based Ionic Liquids such as [bmim][PF₆] and [bmim][BF₄] than other gases such as ethylene, ethane, methane, oxygen, argon, nitrogen, carbon monoxide and hydrogen. Ionic Liquids have the potential to capture CO₂ from gas mixtures, particularly flue gases and natural gas [107].

C.5. OXYGEN SEPARATION TECHNOLOGIES

Pure oxygen can be required for several units of the IGCC with Hydrogen co-production process. For instance, it can be used as coal gasification oxidant agent instead of air, increasing the cold gas efficiency of the gasifier. Or it can be necessary for combustion with pure oxygen if oxycombustion technology is applied for CO₂ capture. Usually, the separation of the oxygen from the air is directly responsible of an important part of the ancillary power consumed by the power plant. In addition, low oxygen purities cause efficiency losses because of processing and/or compression of the inert gases that, together with the oxygen are mixed with the fuel. In general, oxygen separation efficiency has a major impact on the global efficiency of the power plant.

Commercial technologies for oxygen separation are:

1. Cryogenic Air Separation Unit (ASU)
2. PSA/VSA
3. Membranes (Polymeric and Ion transport)

The selection of the oxygen technology has to be based on the purity of oxygen required, on the amount of oxygen that has to be produced and on the energy consumed for ton.

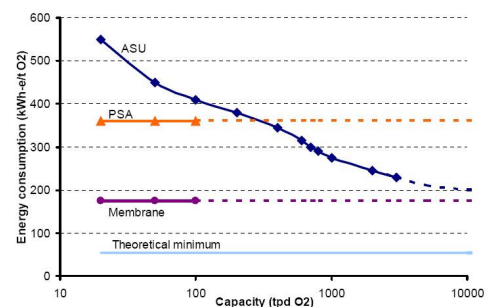


Figure 49 Oxygen separation capacity [108]

CRYOGENIC AIR SEPARATION UNIT

This method is based on a distillation process at cryogenic temperatures. It is the only process that has been applied for large scale oxygen production. The air is pressurized to 5-6 bar and fed into one or more fixed bed adsorbers with molecular sieve materials where CO₂, N₂O, trace hydrocarbons and water are removed. Usually two vessels configuration is used to allow adsorption in one vessel while the other is regenerated. Bed is regenerated via pressure swing or temperature swing using a low pressure waste nitrogen stream[67]. Air is further cooled and fed into a double distillation column, one operating at high pressure and the other at low pressure. Pure oxygen and nitrogen fractions are obtained at near atmosphere pressure.

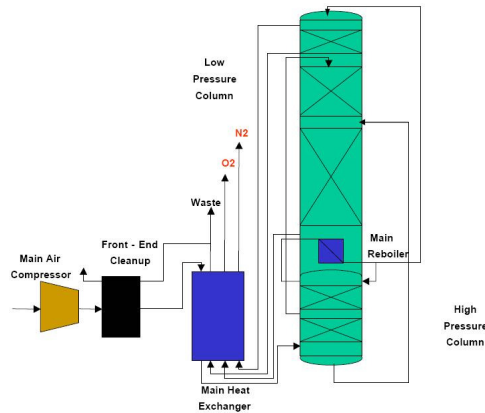


Figure 50 ASU [109]

If high purity is required argon must be removed from the distillation system at an intermediate point. If high pressure oxygen is required then is advisable the use of a "LOX boil" cycle (LOX: Liquid Oxygen). In this cycle, part of the feed air is compressed to higher pressure than normal. The heat is extracted from the air by condensation and is used to warm and vaporize the oxygen to just above the required pressure.

PRESSURE AND VACUUM SWING ADSORPTION

The operation mode of this technology has been already explained in the section 5. about CO₂ capture, but in this case, instead of feeding shifted gas for hydrogen purification, the feed flow is air. Operating pressure is about 7bar and oxygen adsorbent material is carbon molecular sieve, zeolitas, silica...

Vacuum Swing Adsorption is used when the required oxygen purity is low (90-93%). Required inlet pressure is lower than with PSA and less air has to be treated to obtain the same amount of oxygen

MEMBRANES

Polymeric membranes can separate oxygen from nitrogen via diffusion selectivity. Main advantages of a membrane separation system are the low capital cost, the fast start-up due to the near ambient operation and the flexible flow and purity that can be achieved. However the maximum purity of oxygen is relatively low because CO₂ and water are more permeable than oxygen for most membrane materials.

Ion transport membranes are dense inorganic membranes based on ceramic materials as Fluorite, Perovskites, Pyrochlores or Brownmillerite. They have the capacity of diffusing oxygen ions through their structure when a partial pressure or a voltage gradient is applied. Pressurized air temperature is between 700 °C and 950°C [108]. Compared with polymeric membranes, ionic transport membranes afford a more pure oxygen and it requires less start-up time but they are still in an early development stage.

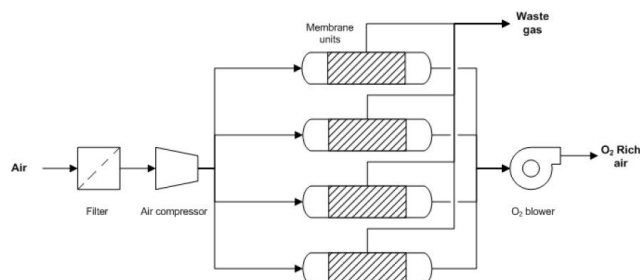


Figure 51 Membrane configuration [108].

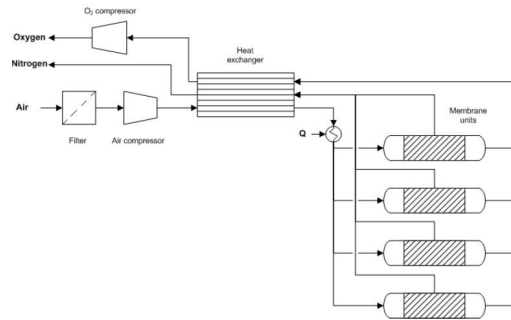


Figure 52 Ion transport membranes configuration [108].

INNOVATIVE PROCESSES

Chemical absorption of oxygen into molten salt is one of the processes in development stage. Absorption/desorption cycle occurs in a two columns configuration at pressures varying from 1 to 10 bar. Before entering into the absorption column, air flows through an adsorbent bed where nitrogen, CO_2 and water are removed in order to avoid salts formation in the column. Clean air is heated to 500-600°C before entering in the vessel where oxygen reacts with the molten salt. Besides possible corrosion problems, the amount of heat necessary for regeneration is one of the disadvantages of this process. On the other hand highly pure oxygen is obtained.

C.6. HYDROGEN SEPARATION TECHNOLOGIES

As for oxygen separation, hydrogen separation technologies are based on cryogenic processes, PSA or membranes.

PSA and membranes based technologies have been explained in the section 5 of this chapter about CO_2 capture. Only polymeric membranes are commercialized for hydrogen separation. The purity of the obtained hydrogen depends on the composition of the original gas, on the effective area of the membrane and on the feed pressure, besides of the characteristics of the membrane. A 80-92% of the Hydrogen can be recovered under optimum operating conditions.

The main characteristics of the cryogenic process are similar to the ones already explained in the Section 6 where ASU is described. As for oxygen, cryogenic hydrogen separation is based on the different volatility of the compounds of the stream. However, in this case, the feeding pressure for optimal operation is between 20-83 bar. The cryogenic process is most attractive when the hydrogen content of the feed is low (30 to 50 vol-%), when the expansion of hydrocarbons provides the necessary cooling without external refrigeration

For the selection of the separation the criteria that have to be considered are summarized in the next table:

FACTORS	PSA	POLYMERIC MEMBRANE	CRYOGENIC
Minimum feed H_2 %	50	15	15
Feed pressure (bar)	10-69	14-138	14-83
H_2 purity %	99.9+	98 max.	97 max
H_2 recovery %	Up to 90	Up to 97	Up to 98
H_2 product pressure	Approximately feed	Much less than feed	Approximately feed
Feed pre-treatment	No	Yes	Drying and removal of compounds that may freeze in the system
Flexibility	Very high	High	Average
Reliability	High	High	Average
Ease of expansion	Average	High	Low

Table 37 Hydrogen separation methods . Adapted from [110]

C.7. GAS TURBINES (GT)

BURNING HYDROGEN RICH GASES

Most of the industrial gas turbines are designed to work with natural gas. Nowadays most of them are ready to burn gases with lower heating value as the gas obtained from coal gasification in IGCC power plants. However, the high hydrogen content in the gasification gas after shift reaction complicates the use of this fuel in conventional gas turbines that in general are designed originally for operation with natural gas (NG). Shift reaction has to be carried out before combustion in plants where CO₂ pre-combustion removal is performed. Once CO₂ is withdrawn from the gas, the remaining gas is composed mainly by hydrogen (>85% mol). Compared NG, hydrogen has a higher heating value, higher heat transfer coefficient and it has a high temperature of combustion. As a result, NO_x levels are higher than with NG and the heat transfer coefficient affects the performance of the cooling system[111].

Property	Hydrogen	Methane
Adiabatic flame temperature in air (K)	2380	2236
Auto-ignition temperature in air (K)	858	813
Density at standard conditions (NTP) g/m ³	83.7	651.2
Detonation limits in air (Vol %)	18 - 59	6.3 - 13.5
Detonation velocity in air, NTP, (m/s)	1.5 - 2.1	1.4-1.6
Flame velocity in air (NTP) (m/s)	0.26-0.32	0.037-0.045
Flammability limits in air (Vol %)	4-75	5.5-15
Heat of combustion - low/high - (kJ/g)	120/141	50/55.5
Minimum ignition energy in air (mJ)	0.02	0.29
Molecular weight	2	16
Quenching distance in air, NTP, (mm)	0.5	2.5
Thermal conductivity NTP (mW/cmK)	1.9	0.33

Table 38 Hydrogen vs Methane properties [112]

There are several options for NO_x emissions control:

1. **Lean pre-mixed combustion:** The amount of air fed in the combustor is above the stoichiometric levels in the combustion primary zone. It is effective for NO_x control because of the lower flame temperature. However experimental works have reported that when hydrogen is burned the flame becomes highly instability and there is a risk of suffering flash backs, flow off... Increasing gas velocity and/or adjusting and redesigning the air flow injection system could help to control the instabilities[113].
2. **Pre-mix and catalytic combustion:** the combination of both technologies results in very low NO_x emission levels. However, pre-mixing hydrogen causes problems because of the greater flammability limits and the lower ignition temperatures. This technology is being object of many researches trying to solve the problems with pre-mixer and to control the wall temperatures of the catalytic bed.
3. **Dilution with steam or nitrogen:** the use of diffusion burners allows the dilution with steam or nitrogen to reduce the flame temperature therefore the NO_x emissions. Nitrogen dilution is used if nitrogen can be obtained from another part of the process (i.e.ASU)
4. **Selective catalytic reaction with ammonia:** (See section 5.CO₂ capture via chemical absorption with amines). The main inconvenience of this process is the important cost when a considerable amount of gas has to be treated.

Paolo Chiesa et al. [111] state that the dilution of the fuel with steam or nitrogen is the most convenient option to control NO_x emissions rather than catalytic combustion or removal from exhaust gas via ammonia injection. The use of steam for dilution ensures lower compression energy consumption than for nitrogen and an increased enthalpy drop in the turbine because of the variation of the heating capacity of the mixture.

Other problem that appears when operating with hydrogen is related with the matching between the compressor and the expander. Since hydrogen has such a high calorific value compared with natural gas, the mass flow entering into the turbine is lower when using this gas. However, because of the lower molecular weight of the hydrogen, the volumetric flow is larger than with natural gas. In addition, the need to dilute the hydrogen to reduce NO_x levels can result in the volumetric flow very increased. This can make the turbine becoming choked.

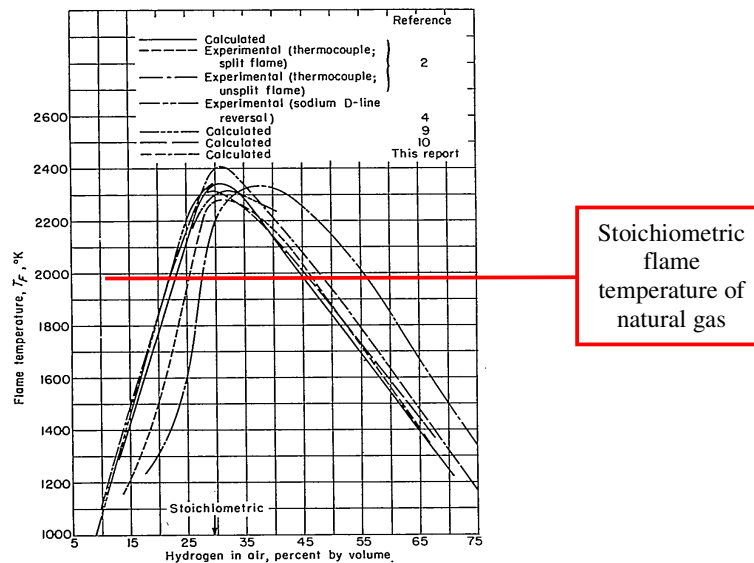


Figure 53 Flame temperature of Hydrogen

Chiesa et al. propose three operating approach to restore the compressor/turbine matching.

1. Keeping the compressor operating point and reduce the Turbine Inlet Temperature (TIT). In this case the energy input is reduced therefore the volumetric flow is reduced and the turbine can work as designed. However the loss of efficiency of the combined cycle due to the TIT and TOT reduction makes of this method a non advisable option.
2. Increased pressure ratio: to adapt the operating conditions to the larger gas flow for the same airflow and turbine geometry. As the mass flow of air is not reduced, the power generated is higher. If it is necessary to avoid surge limit more high pressure stages must be added to the compressor
3. Variable Inlet Guide Vane(VGV) operation: at the entrance of the compressor the inlet guide vanes control the inlet air flow by variation of the angle in order to control compressor surge during start-ups of part load operation. This strategy for burning hydrogen in the gas turbine consists on decreasing the amount of air used for combustion by decreasing the VGV while pressure ratio and TIT are kept at design point. The turbine operating point is not affected and the compressor efficiency remains constant. Besides, the GT output is increased because the lower required power for compression, however, it should be considered power needed to compress the nitrogen if this is use for dilution. The main disadvantage of this operation mode is the more limited part load operation, given that VGV are already closed for full load.

The third inconvenience of burning hydrogen on gas turbines that is analyzed by Chiesa et al. is the performance of the blade cooling considering the increased heat transfer coefficient and the fact that this situation get worst if operating pressure ratio is increased. A higher pressure ratio not only increases more the heat transfer coefficient but the cooling air temperature. The only feasible solution to this problem is to decrease the TIT in order to keep the blade temperature under its admissible limits. This reduction will have an important penalty on the efficiency of the cycle if increased pressure ratio strategy is adopted. Other approach is to cool the cooling air by absorbing the heat in feed water to the steam cycle.

Nowadays there is some practical experience on burning hydrogen. A process gas containing 85%vol to 95%vol hydrogen is being burnt in the GE gas turbine MS6001B (40MW) at the Daesan Petrochemical Plant in Korea since 1997. The maximum values of hydrogen concentration burned in an IGCC plant are 62%-65% vol for a GE MS6000B turbine at Schwarze Pumpe power plant and 45%-47%vol of H₂ for a GE 209E at the Vresova plant in Czech Republic [114]. General Electric is currently involved in the development of the FB gas turbine available for syngas operation in early 2009. GE assures that the new FB class will show high performance burning hydrogen given that the operation temperature is higher than for current F-class while keeping low NO_x levels thanks to the close- loop steam cooling on the first-stage nozzle that is exposed to higher temperatures[115]. Besides GE is participating in the U.S. Department of Energy's multi-phase hydrogen turbine program where the objective is to design and develop fuel-flexible (burning coal derived hydrogen or syngas) gas turbines, meeting DOE goals, such as "NO_x less than 3 ppm by 2015"[116]

Siemens is participating at the Advanced Hydrogen Turbine Development Project whose objective is to design and develop a fuel flexible advanced gas turbine for IGCC applications. The starting point for the development of the new gas turbine is the SGT6-6000G because of its high performance as well as low capital cost [117]. Mitsubishi has experience on burning oil refinery offgas containing 80-90%vol of hydrogen [118]. Besides, they are developing a 1700°C class gas turbine for combined cycles with high performance compressor, low NO_x combustor and a turbine capable of withstanding an inlet temperature of 1700°C [119].

REFERENCES

- [1] Coal geology and Coal Technology. Colin R. Ward. Blackwell Scientific Press, 1984
- [2] IEA Coal glossary <http://www.eia.doe.gov/cneaf/coal/page/gloss.html>
- [3] Status of Sponge Iron Industry in Jharkhand - By V. D. Manjrekar Geo-Mining Consultant. Steel World Feb. 2005 pages 8-12.
- [4] Combustion and Gasification of Coal. A. Williams, M. Pourkashanian, J.M. Jones, and N. Skorupska. Taylor & Francis, 29 W. 35th St., New York, NY 10001. 2000. 263 pp
- [5] Some aspects of measurement, interpretation and practical use of results from solid fuel reactivity studies . Jacek Zelkowski. Energy, Volume 26, Number 12, December 2001 , pp. 1185-1195(11)
- [6] http://euracoal.be/newsite/pdf/publication/coal_industry_2005.pdf
- [7] <http://www.wou.edu/las/physci/GS361/Fossil%20fuels/Coal.htm>
- [8] Structural Evolution of Matched Tar-Char Pairs in Rapid Pyrolysis Experiments. Pugmire, R. J., M. S. Solum, D. M. Grant, S. Critchfield and T. H. Fletcher, Fuel 70: 414-423 (1990)
- [9] International classification of in-seam coals- Economic commission for Europe committee on sustainable energy. United Nations
- [10] A practical approach to predicting ash deposition. David P. Kalmanovitch, DB Riley, Inc., Worcester, MA
- [11] Comparison of inorganic constituents in three low-rank coals. Benson S.A.; Holm P.L. Ind Eng Chem Prod Res Dev 24 (1985), pp. 145-149
- [12] Coal Properties, Sampling and Ash characteristics . Rod Hatt; See also:
<http://www.coalcombustion.com/PDF%20Files/Coal%20Properties103.pdf>
- [13] Solid wastes from coal-fired power plants - Use of disposal on agricultural lands. Terman, G.L. Tennessee Valley Authority Bulletin Y-129, (1978) Natl. Fert. Devel. Center, Muscle Shoals, AL.
- [14] Sedimentary facies of the coal-bearing Westphalian A and B north of the Wales-Brabant High. In `European Coal Geology Guion P.D., Fulton I.M. and Jones N.S. (1995) (Whateley, MKG and Spears, DA editors), Geol.Soc.Spec.Publ. 82, 45-78.
- [15] Classification of sediments and sedimentary rocks C.R. Hallsworth and RW O'B Knox British geological survey
- [16] Euracoal <http://euracoal.be/newsite/membresst.php>
- [17] BP Statistical Review of World Energy June 2008. See also:
<http://www.bp.com/productlanding.do?categoryId=6929&contentId=7044622>
- [18] Pyrolysis of fine coal particles at high heating rate and pressure. Christopher John Mill . PhD thesis. University of New South Wales 2000
- [19] Nitrogen evolution and soot formation during secondary coal pyrolysis. Haifeng Zhang. Dissertation at the Brigham Young University. April 2001.
- [20] Review of the kinetics of pyrolysis and hydropyrolysis in relation to the chemical constitution of coal H. Jüntgen 1983 FUEL Vol 63
- [21] Devolatilization and combustion characteristics of coal particles. S. C. Saxena. Prog. Energy. Combust. Sci. 1990, Vol. 16, pp. 55-94
- [22] The Structure and Reaction Processes of Coal Door K. Lee Smith, L. D. Smoot, T. H. Fletcher, R. J. Pugmire, Bijdrager K. Lee Smith. Ed. Springer, 1994
- [23] Progress in coal pyrolysis. P. R. Solomon, T. H. Fletcher and R. J. Pugmire. Advanced fuel research Fuel Volume 72, Issue 5, May 1993, Pages 587-597
- [24] Relation between tar and extractables formation and crosslinking during coal pyrolysis . Suuberg, E.M., Unger, P.E., and Larsen, J.W., Energy & Fuels, 1, 305, (1987)
- [25] Pyrolysis of Argonne Premium coals: activation energy distributions and related chemistry. Burnham A.K., Oh M.S., Crawford R.W., Samoun A.M. Energy and Fuel, 3, 42 (1989)
- [26] The Conversion of Coal into Oils Dr. Franz Fischer . Edited by R. Lessing (1925)
- [27] Assessment of the commercial potential for small gasification combined cycle and fuel cell systems Prepared by HM Associates Inc. and TFB Consulting. Prepared for US Department of Energy. Office of Fossil Energy. Office of Coal and Power Systems. March 2003
- [28] Perry's Chemical Engineers' Handbook 7th edition. Robert H. Perry and Don W. Green. Mc Graw Hill International Editions 1998.
- [29] Gasification -Versatile Solutions. DOE's Gasification Program Overview. Version N August 21, 2007 Gary J. Stiegel . See also: <http://www.naseo.org/events/annual/2006/presentations/Steigel.pdf>
- [30] Gasification Christopher Higman and Maarten van der Burgt. Published by Elsevier ISBN 0-7506-7707-4, 2003.
- [31] The Siemens Gasification Process and its Application in the Chinese Market. Klaus-Dieter Klemmer. Siemens. 2006 Gasification technologies conference.

- [32] Coal gasification for advanced power generation. Andrew J. Michener. Fuel Volume 84, Issue 17, December 2005, Pages 2222-2235
- [33] Hot Dechlorination and Hot Desulfurization of Reducing Gases with lime pellets. Fusch, Y. and Schwerdtfeger, K.
- [34] High Temperature Gas Cleaning. Eds Schmidt, E. et al, Inst fur Mech Verf. Und Mech, Univ Karlsruhe. Germany (1996).
- [35] Gasification Process Selection- Trade-offs and Ironies Neville Holt – EPRI. Gasification Technologies Conference 2004. See also: http://www.gasification.org/Docs/Conferences/2004/30HOLT_Paper.pdf
- [36] Initial review and evaluation of process Technologies and systems suitable for Cost-efficient Medium-Scale gasification for Biomass to liquid fuels Ingemar. Olofsson, Anders Nordin and Ulf Soderlind. Energy Technology & Thermal Process Chemistry. University of Umea, S-901 87 Umea, Sweden. ISSN 1653-0551 ETPC Report 05-02
- [37] Transport Gasifier IGCC Base Cases, US DOE/ NETL Report PED-IGCC-98-006 September 1998 Latest Revision June 2000
- [38] Coal resources, properties, utilization, pollution. Davidson R.M. O. Kural (Ed.) Istanbul Technical University, Istanbul, 1994, pp.494. ISBN 975-95701-1-4
- [39] German developments in biomass gasification . Eckhard January 31, 2006 in Coal-to-Liquids (CTL)
- [40] Gasification of solid and liquid fuels for power generation. Technology status report.US Department of Trade and Industry. December 1998. TSR008
- [41] http://www.mhi.co.jp/power/e_power/techno/igcc/index.html
- [42] http://www.coptechnologiesolutions.com/egas/process_overview/index.htm
- [43] Pressurized entrained flow gasification and its application to combined-cycle power plants S H. Ch. Pohl J. K. Rohm GKT* Gesellschaft für Kohle-Technologie, mbH Essen, Federal Republic of Germany. See also: http://www.fischer-tropsch.org/DOE/_conf_proc/Electric%20Power%20Research/4257-sr/epri_ap-4257-sr-B-16.pdf
- [44] CFD Modeling For Entrained Flow Gasifiers. Mike Bockelie, Martin Denison, Zumao Chen, Temi Linjewile, Connie Senior, Adel Sarofim., and Neville Holt. Gasification Technologies Conference 2002. DOE Vision 21 Program.
- [45] IGCC Power Plants – EPRI Design & Cost Studies EPRI/GTC Gasification Technologies Conference San Francisco, CA October 6, 1998 (Modified October 30, 1998) Neville Holt EPRI – Energy Conversion Division
- [46] Integrated Drying and Gasification : Technology for Power Generation Brown Coal and Biomass.Terry Johnson and Brian Young. See also: <http://www.aie.org.au/material/NatConf99/IDGCC.ppt>.
- [47] Combustion/Gasification in the Lurgi Circulating Fluid Bed L. Piass; H. Beisswenger; H. Lienhard;H. Bierbach Lurgi GmbH, Frankfurt am Main. See also: http://www.fischer-tropsch.org/DOE/_conf_proc/Electric%20Power%20Research/4257-sr/epri_ap-4257-sr-B-10.pdf
- [48] http://www.netl.doe.gov/technologies/coalpower/cctc/ccpi/project_briefs/CCPI_SouthernCompanyGasifier.pdf
- [49] http://www.stoner.com/PDF/BGL_Gasifier_DS.pdf
- [50] Wood gas as engine fuel. Mechanical Wood Products Branch. Forest Industries Division FAO Forestry Department. Mechanical Wood Products Branch. Forest Industries Division. See also: <ftp://ftp.fao.org/docrep/fao/t0512e/t0512e00.pdf>
- [51] Matching gasifiers to coals Anne-Gaëlle Collot IEA Clean Coal Centre. CCC/65, ISBN 92- 9029-380-2, 63 pp., October 2002,
- [52] Assesment of the quality of Indiana coals for Integrated gasification combined cycle performance: Analysis of the existing data and propolsal of new research Mastalerz, M., Drobnia, A., Rupp, J., Shaffer, N. Final report to the Center for Coal Technology Research. Indiana Geological Survey. Indiana University (2005)
- [53] Hydrogen from Coal Multi-Year RD&D Plan DOE September 26, 2005
- [54] Control of pollutants in flue gases and fuel gases, 2nd edition Ron Zevenhoven and Pia Kilpinen (2002) Report TKK-ENY-4 ISSN 1457-9944, ISBN 951-22-5527-8
- [55] <http://www.mindfully.org/Nucs/Firing-Range-Air-Cleaning1mar85.htm>
- [56] APTI Virtual classroom. Lesson4 See also: <http://yosemite.epa.gov/oagps/EOGtrain.nsf/homeform?openform>
- [57] <http://www.forbesgroup.co.uk/product.php/81/0//b88cd69f31a58bda50a09911b4080d6c> "Air Pollution Technology Fact Sheet" EPA
- [58] Gas purification. Kohl A., Nielsen R.. 5th Ed. Gulf publishing Company.Book division. P.O.Box 2608, Houston, Texas.
- [59] Advanced coal gasification technical analyses. Appendix 1: Technology reviews Cover, A.E. ; Hubbard, D.A. ; Jain, S.K. ; Shah, K.V. 1986. OSTI Technical Report. Report number PB-86-203148/XAB.
- [60] Review and Evaluation of Alternative Chemical Disposal Technologies (1996). Magee R. S.
- [61] Stretford plant operating Experience at DOFASCO. Penderleith Y. Proceedings of the Symposium on Treatment of Coke-Oven Gas. McMaster University, Hamiston, Ontario, Canada, May 26 1977
- [62] Air pollution control technology in Japan. Exhaust Gas Treatment Equipment www.gec.jp
- [63] Handbook of gasifiers and gas treatment systems. Raj D Parekh. WD-TR-82/008-010 Sep. 1988, pp. 2A.24-2A.41
- [64] Removal of hydrogen sulfide from biogas using cow-manure compost. Steven McKinsey Zicary. Thesis at the Faculty of Cornell University. (2003)

- [65] Engineering standard for process design of gas treating units. Part1- Process design of gas sweetening units 1997. IPS-E-PR-551 Iranian Petroleum Standards.
- [66] Contaminants in amine gas treating. Randy Haws CCR Technologies Inc. 11375 West Sam Houston Pkwy South. Suite 201. Houston, Texas 77031
- [67] Recovery of CO₂ from flue gases: Commercial Trends Dan G. Chapel, Carl L.Mariz. Canadian Society of Chemical Engineers annual meeting. 1999.
- [68] Advanced Gas Treating to Enhance Producing and Refining Projects using FLEXSORB SE* Solvents Robert B. Fedich, David S. McCaffrey, Jr., and James F. Stanley
- [69] CO₂ recovery from flue gas by the Benfield process. Grover, B.S., and E.L. Bergen. Petroenergy 1983, Houston, Texas
- [70] SO_x-NO_x-Rox Box™ Flue Gas Cleanup Demonstration Project . The Babcock & Wilcox Company ;Ohio Edison Company, Ohio Coal Development Office Electric Power Research Institute,Norton Company
- [71] Hot gas granular moving bed filters for advanced power systems. J Smid, C Y Peng and H T Lee. Energy & Resources Laboratories, Industrial Technology Research Institute
- [72] Integrated hot fuel gas cleaning for advanced gasification combined cycle processes. A.J. Minchener. CRE Group Limited
- [73] Development of disposable sorbents for chloride removal from high temperature coal-derived gases. Oct.1993- June 1999 Gopala Krishnan SRI InternationalRaghubir Gupta Research Triangle Institute
- [74] Desulfuración de gas de síntesis a alta temperatura y presión por absorción en óxidos regenerables. Perales Lorente, José Francisco
- [75] A study on sulphidation and regeneration of Z-Sorb III sorbent for H₂S removal from simulated ELCOGAS IGCC syngas. Sanchez-Hervas J.M.; Otero J. ; Ruiz E.
- [76] Hot gas desulfurization with sulphur recovery. Yiding Zeng. Douglas P. Harrison
- [77] CO₂ capture- post combustion flue gas separation S.Wong
- [78] <http://ect.jmcatalysts.com/technologies-scr-ammonia.htm>
- [79] "An Economic Scoping Study for CO₂ Capture Using Aqueous Ammonia, J. Ciferno, P. Dipietro, and T. Tarka, US DOE/NETL Report, February 2005;
- [80] Aqua ammonia process for simultaneous removal of CO₂, SO₂ and NO_x. Resnick K.P., Yeh, J.T.,Pennline, H.W International Journal of Environmental Technology and Management. Vol.4, Nos.1/2 2004)
- [81] Carbon dioxide capture technology for the coal-powered electricity industry : a systematic prioritization of research needs. Esber, George Salem Massachusetts Institute of Technology. Technology and Policy Program http://sequestration.mit.edu/pdf/Salem_Esber_Thesis.pdf
- [82] Dry Regenerable Carbonate Sorbents for Capture of Carbon dioxide from Flue Gas. Coker D., Figueroa J., Green D.A., Gupta R.P., McMichael W.J., Nelson T.O., Portzer J.W. Fourth Annual Conference on Carbon Capture and Sequestration, May 2-5, 2005, Washington D.C.
- [83] Carbon Dioxide Capture by Absorption with Potassium Carbonate. Cullinane J.T., Oyeneke B.A., Lu J. , Rochelle G.T. NETL funded project, University of Texas, Austin 2002
- [84] New Solvents Based on Amino-Acid Salts for CO₂ capture from Flue Gases. Feron PHM, Asbroek N. 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9,2004 Vancouver. Canada
- [85] CO₂ capture from flue gas using amino acid salt solutions Jacco van Holst, Patricia. P. Politiek, John P. M. Niederer, Geert F. Versteeg
- [86] CO₂ Capture and Reuse CANMET Energy. Thambimuthu, K. V. et al. (2002) Technology Centre, Natural Resources Canada IEA Greenhouse Gas R&D Programme Cheltenham, United Kingdom
- [87] PSA Operation and Controls Rudolf HuyckeUOP N.V. Rudolf Huycke UOP N. 4th European Technical Seminar on Hydrogen Plants - Lisbon - October 2003
- [88] Carbon Sequestration Research and Development DOE's Office of Fossil Energy and Office of Science 1999
- [89] Including CO₂ removal in power plants. Giampaolo Manfrida.
- [90] Recent developments in CO₂ removal membrane technology David Dortmund. Kishore Doshi.
- [91] Selection of a Hydrogen Separation Process. Geoffrey Q. Miller, and Joerg Stöcker
- [92] A Review of Carbon Dioxide Selective Membranes. NETL. Dushyant Shekhawat, David R. Luebke and Henry W. Pennline
- [93] Prospects for hydrogen coal. Anne-Gaëlle Collot CCC/78 ISBN 92-9029-393-4, 76pp. Dec.2003
- [94] High temperature membranes in power generation with CO₂ capture. Rune Bredesen, Kristin Jordal, Olav Bolland
- [95] Ceramic membranes for Gas separation-Recent Developments and State of the Art. H.A. Meinema, R.W.J.Dirrix, H.W. Brinkman, R.A.Terpstra, J.Jekerle, P.H.Köstors
- [96] Status review on membrane systems for hydrogen separation S.C.A. Kluiters
- [97] Facilitated transport of carbon dioxide through supported liquid membranes of aqueous amine solutions. Teramoto M., Nakai K. Ohnishi N., Huang Q., Watari T., Matsuyama H. Ind. eng. Chem, 35, 538-545, 1996.
- [98] Development of CO₂ separation membranes (1) Facilitated transport membrane., Okabe K., Matsumiya N., Teramoto M. In Greenhouse Gas Control Technologies. J.Gale and Y. Kaya (eds.),Elsevier Science, Ltd.,United Kingdom, 1555-1558 2003.
- [99] Selective CO₂ separation from CO₂-N₂ mixtures by immobilised carbonate-glycerol membranes. Chen H., Kovvali A.S., Majumdar S. Sirkar K.K, Ind. Eng. Chem.,38, 3489-3498 , 1999

- [100] Dendrimer liquid membranes: CO₂ separation from gas mixtures. Kovvali A.S. , Sirkar K.K., Ind. Eng.Chem., 40, 2502-2511. 2001
- [101] Polyelectrolyte membranas for acid gas separations. Quinn R., Laciak D.V., Journal of Membrane Science, 131, 49-60. 1997
- [102] Near Zero emission technology for CO₂ capture from power plants. J.W.Dijkstra J. van der Marel, B.C.C. van der Zwaan, F.P.J. M. Kerkhoff
- [103] Carbon Dioxide Reuse and Sequestration:The State of the Art Today Sally Benson (LBNL), Thomas Dorchak (NETL), Gary Jacobs (ORNL), James Ekmann (NETL), Jim Bishop (LBNL), and Thomas Grahame (DOE)
- [104] Applications of chemical-looping combustion with capture of CO₂ Tobias Mattisson ,Anders Lyngfelt Chalmers University of Technology
- [105] Chemical looping combustion of coal in interconnected fluidized beds Shen LaiHong , Zheng Min , Xiao Jun , Zhang Hui and Xiao Rui
- [106] Integrated Hydrogen and Power Production with CO₂ capture using Chemical Looping Reforming –Redox Reactivity of Particles of CuO, Mn₂O₃, NiO, and Fe₂O₃ Using SiO₂ as a Support. Zafar Q., Mattisson T. Gevet B., Industrial & Engineering Chemistry Research, 2005. 44(10): p3485-3496
- [107] Feasibility of using ionic liquids for carbon dioxide capture Jennifer L. Anthony, Sudhir N.V.K. Aki,Edward J. Maginn and Joan F. BrenneckeDepartment of Chemical and Biomolecular Engineering,University of Notre Dame
- [108] Techno-economic assessment for power generation options for Australia. Louis Wibberley, Aaron Cottrell, Doug Palfreyman, Peter Scaife, Phil Brown
- [109] ITM Oxygen: The New Oxygen Supply for the New IGCC Market Phillip A. Armstrong; Douglas L. Bennett; E.P. (Ted) Foster; VanEric E. Stein
- [110] Selection and Revamp of Hydrogen Purification Processes. Michael Whysall, Kathy Ward Picioccio. UOP LLC.
- [111] Using Hydrogen as Gas Turbine Fuel. Paolo Chiesa. Giovanni Lozza and Luigi Mazzocchi
- [112] Use of hydrogen combustion for power generator. D.CWalther,A.C Fernandez-Pello, R.Dibble
- [113] Characteristics of Hydrogen Combustion in an Experimental Lean Premixed Combustor. Takeyuki Kishi, Katsuhide Hiraoka, Masaru Ikame, Kazuyoshi Harumi, Hideyuki Shiota, Hideyuki Oka
- [114] Power Generation Markets Driving Fuel-Flexible Solutions, Robert M. Jones, Jean Michel Bisseaude, Michel Moliere
- [115] The 7FB: The next evolution of the F gas turbine. Roberta Eldrid Lynda Kaufman Paul Marks
- [116] IGCC: The race is on. Turbomachinery International . Kalyanaraman K... July/August 2006
http://findarticles.com/p/articles/mi_qa5385/is_200607/ai_n21397218
- [117] Advanced hydrogen turbine development . Bancalari E.,Chan P. and Diakunchak I.S.. Siemens power Generation Inc,2006
- [118] CO₂ Emission Reduction Method Through various Gas Turbine Fuel Applications . Komori T., Shiozaki S., Yamagami N., Kitauchi Y., Akizuki W.. Mitsubishi Heavy Industries, Ltd. Technical Review Vol. 44 No. 1 (Mar. 2007).
- [119] Development of High Efficiency Gas Turbine Combined Cycle Power Plant.. Ishikawa M., Terauchi M., Komori T., Yasuraoka J.. Mitsubishi Heavy Industries, Ltd. Technical Review Vol. 45 No. 1 (Mar. 2008)

European Commission

EUR 23661 EN– Joint Research Centre – Institute for Energy

Title: Technologies for Coal based Hydrogen and Electricity Co-production Power Plants with CO₂ Capture

Author(s):

Carolina García Cortés

Evangelos Tzimas

Stathis Peteves.

Luxembourg: Office for Official Publications of the European Communities

2009 –72 pp. – 21 x 29.7 cm

EUR – Scientific and Technical Research series – ISSN 1018-5593

ISBN 978-92-79-11076-4

DOI 10.2790/23969

Abstract

Integrated Gasification Combined Cycle (IGCC) plants allow the combination of the production of hydrogen and electricity because coal gasification process produces a syngas that can be used for the production of both commodities. A hydrogen and electricity power plant has been denominated as HYPOGEN.

This report starts by reviewing the basics of the coal gasification process and continues by trying to map all the technological options currently available in the market as well as possible future trends that can be included in a HYPOGEN system. Besides, it offers an overview of the operating conditions and outputs of each process in order to provide the modeller with a useful information tool enabling an easier analysis of compatibilities and implementation of the model.

How to obtain EU publications

Our priced publications are available from EU Bookshop (<http://bookshop.europa.eu>), where you can place an order with the sales agent of your choice.

The Publications Office has a worldwide network of sales agents. You can obtain their contact details by sending a fax to (352) 29 29-42758.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.



LD-NA-23661-EN-C